MACHEREY-NAGEL

Water Analysis

Basic principles of Water Analysis

MACHEREY-NAGEL

Starting as a manufacturer of filter paper for laboratory applications in 1911, within the last decades we have become a global company with focus on chemical and molecular biological analysis. In countless applications our products are utilized and help many users in their daily analytical work. Our product segments include filtration, rapid tests, water analysis, chromatography and bioanalysis.

We currently employ about 600 people worldwide, most of which are located in Dueren, Germany, but also in our subsidiaries in Switzerland, France and the USA. We are active in more than 150 countries around the world, thanks to the support of our valuable distribution partners.

Due to scientific research and development, our products belong to the most trusted and reliable analytical systems in the world. Numerous patents and international certifications (i.a. ISO, CE, FDA, EPA) prove this and guarantee you reliable, reproducible results.

MACHEREY-NAGEL has been developing solutions for photometry for more than 35 years. Through a linear device development, continuous improvement, an extraordinary customer proximity and attention to detail we reach highest quality and reliability with our *NANOCOLOR*® analytical system.

Not only quality is highest priority with us. We do everything to offer you, as a user, the best possible support. Our competent customer service team and our distribution partners are always at your disposal. Quality and customer proximity make MACHEREY-NAGEL with the *NANOCOLOR*® analytical system your ideal partner.

With this book covering the basics of water analysis we provide you an important reference book for all questions concerning water analysis and the *NANOCOLOR*® system.

Enjoy reading!

(Head of seminars)

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1. Fundamentals of photometry

In simple terms, photometry is a measurement method for determining the concentration of colored solutions with the aid of electromagnetic radiation (“light”).

The concentration of a certain compound is determined by increase or decrease of the absorbance of the solution, caused by a specific color reaction of the compound to be determined.

The substances to be investigated in photometric measurements may require a pretreatment in order to be fully dissolved. Preliminary solids need to be converted into a dissolved form by appropriate decomposition processes.

It is important to find a color reaction for the parameter to be determined that proceeds quantitatively and specifically. Hence, not every color-producing reaction is suitable for photometric concentration determination.

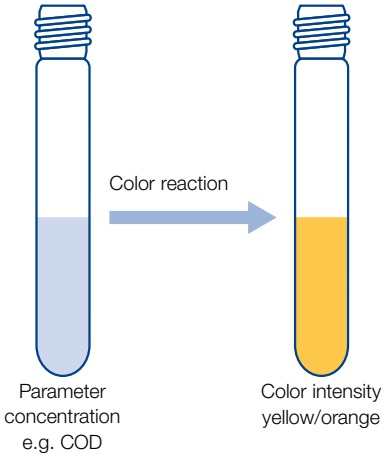

Figure 1: Schematic illustration of a color reaction

1.1 Electromagnetic radiation

Electromagnetic radiation in the range of 190–1100 nm is used for photometric analysis. Light is defined as the range of electromagnetic radiation that is perceptible to human beings. The visible range reaches from approximately 400 to 700 nm.
Figure 2 displays an overview of electromagnetic radiation with the corresponding wavelengths.

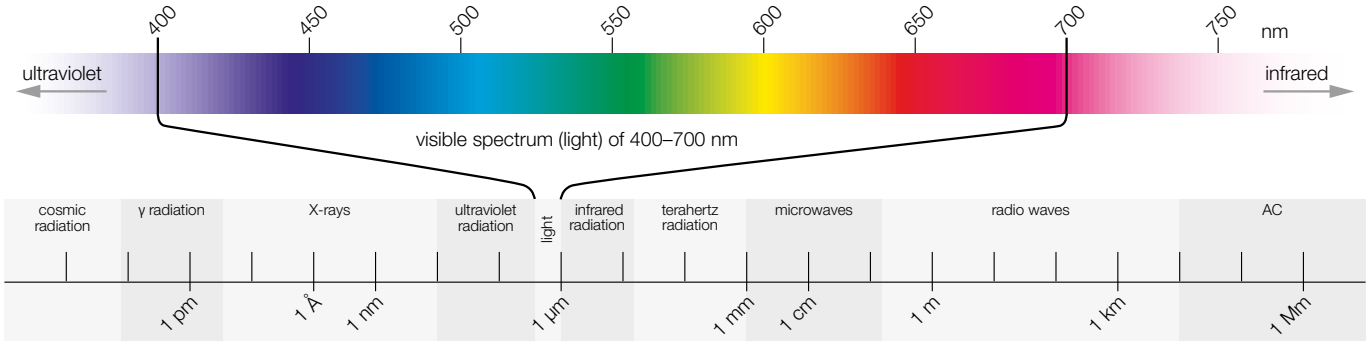

Figure 2: Schematic illustration of electromagnetic radiation

Additionally, UV light is also used (see spectrum) in photometric analyses. Ultraviolet (UV) light is also known as black light and is adjacent to the visual range, with shorter wavelengths below 380 nm. The term UV light, however, is misleading because only a small part of the UV light between 315 nm to 380 nm can be perceived by humans. However, the UV range exceeds human perception by far. Nevertheless, ultraviolet radiation is a form of optical radiation. According to the german norm DIN 5031, Part 7, the UV spectrum comprises the wavelengths from 100 nm to 380 nm, which corresponds to frequencies from 3 PHz to 789 THz. Extreme ultraviolet light follows below this range defined by DIN. The classification of the different types of UV radiation is illustrated in Table 1.

Designation	Abbreviation	Wavelength range
Near UV (“black light”)	UV-A	380–315 nm
Middle UV	UV-B	315–280 nm
Far UV	UV-C-FUV	280–200 nm
Vacuum UV	UV-C-VUV	200–100 nm
Extreme UV	EUV	121–10 nm

Table 1: Classification of ultraviolet radiation by wavelength

Normal glass (soda-lime glass) is impermeable to ultraviolet radiation below 350 nm. Normal round and rectangular cuvettes are therefore not suitable for UV photometry. Borosilicate glass (Jena glass), however, is permeable to UV light down to about 290 nm. Quartz glass is suitable for even shorter wavelengths. Depending on its purity, a permeability down to about 180 nm can be reached.

λ = Wavelength [nm]

The light source used in the visual range is a tungsten halogen lamp, while in the UV range a deuterium lamp is used. The tungsten halogen lamp alone is not able to cover the entire wavelength range. The same applies to the deuterium lamp. Therefore, both lamps are installed in UV/VIS photometers. Both lamps are continuous radiation sources. Figure 3 shows the energy spectra of a tungsten halogen and a deuterium lamp.

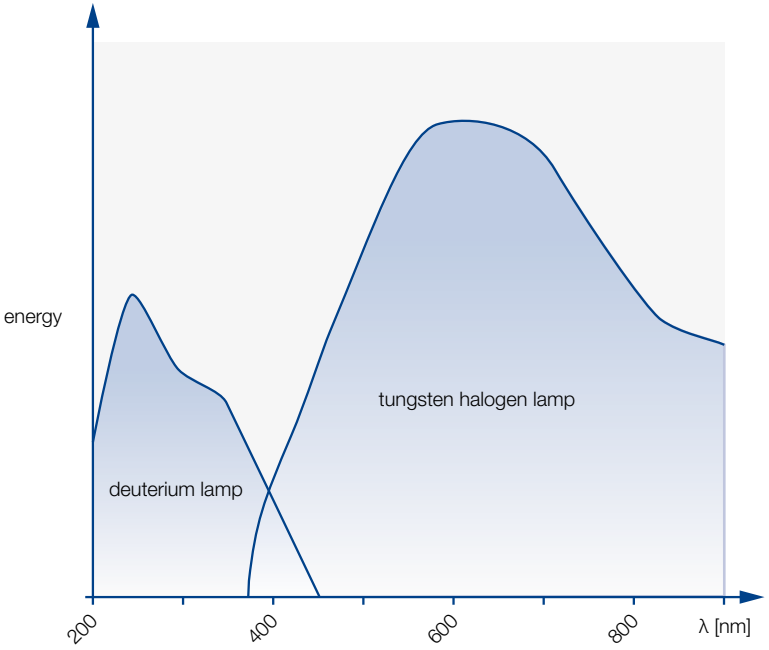

Figure 3: Radiation energies of tungsten halogen and deuterium lamps

The energy of a tungsten-halogen lamp peaks at about 650 nm, while the deuterium lamp exhibits a maximum at about 250 nm.

1.2 Where does color come from?

Light emitted from a radiation source such as a lamp or the sun is generally referred to as white light. It is composed of portions of all wavelengths in the spectral range (polychromatic). By refraction (dispersion) on a prism, white light is split into the individual spectral colors.

Several physical processes play important roles in color perception.

the spectrum of a bright yellow solution shows high transmittance of wavelengths in the green, yellow, orange and red ranges, while the blue and violet ranges are hardly or not at all represented.

Colored solutions absorb their complementary colors. This means that the yellow solution absorbs all violet and blue components of the polychromatic white light, while the other wavelength ranges are transmitted and pass through the test solution unhindered. The yellow color is therefore attributable to the absence of the complementary blue color.

Conversely, this means that violet color is produced by strong absorption in the yellow-green region. Table 2 gives a rough overview of the complementary colors and corresponding wavelengths.

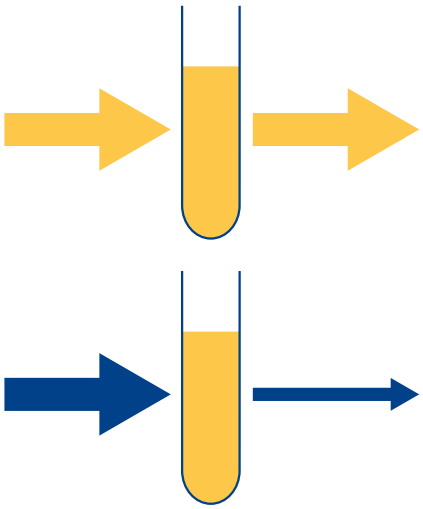

Figure 4: Schematic illustration of light passage with identical and complementary colors of light

Wavelength	Color	Complementary color
< 400 nm	ultraviolet (UV)	not visible
400–435 nm	violet	yellow-green
435–495 nm	blue	yellow
495–520 nm	blue-green (cyan)	red
520–570 nm	green	violet
570–590 nm	yellow	blue
590–650 nm	orange	blue-green (cyan)
650–700 nm	red	blue-green (cyan)
700–750 nm	deep red	blue-green (cyan)
> 800 nm	infrared	black

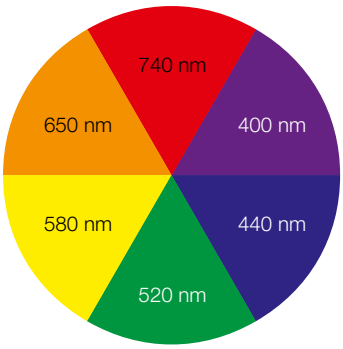

Table 2: Overview of the individual colors of light with the corresponding wavelengths and complementary colors

The human color perception is possible because of visual receptors that are located on the retina. The perceptible wavelength range reaches from 380 to 780 nm. Eventually, color vision is only the triggering of stimuli by light of different wavelengths.

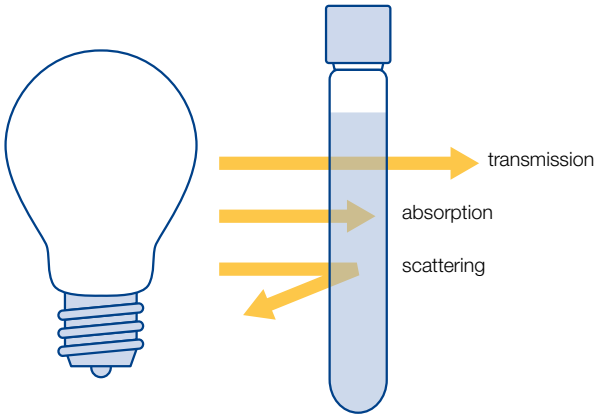

Figure 5: Schematic illustration of transmission, absorption and scattering

Absorption (A) is the loss of energy of certain wavelengths in the sample solution. It depends on the intrinsic color of the test solution. Colloquially, one can say that the absorbed fraction of the radiation is the one that is “swallowed”.

Transmittance (T) is the “permeability” of a sample for specific wavelengths, i.e. the portion that is not absorbed. Occasionally also the term “transparency” rather than transmission is used.

Absorbance (optical density) is a measure of the “quenching” or attenuation of radiation through the sample. The sometimes also used term “extinction” is derived from the Latin word “extinctio” having the same meaning.

Transmittance indicates how much light actually passes through the test solution unhindered. While water has about 100 percent transmittance, the other extreme case (white body) shows 100 percent reflection. In case of complete absorption (black body), by contrast, there is no transmission. The entire incident light (I_0) is absorbed by the substance. Since light is also a form of energy, this explains why under sun light black clothes literally absorb heat and become hot.

As a matter of principle, the exiting light beam is always lower in intensity than the incident beam. This is due to interactions with the cuvette and the sample. The higher the absorption, the lower is the transmission and thereby the intensity of the exiting radiation.

$$I_0 = A + T$$

Absorption (A) = energy lost
Transmission (T) = energy passing through
Absorbance (E) = attenuation

Another concept frequently mentioned in this context is reflection. Reflection is the fraction of light which is reflected at the interface between the glass and sample as well as on the interface between glass and surrounding air. In addition, scattering on suspended particles plays a non-negligible role. Turbidity generally leads to increased measurement values (except in tests with negative measuring direction), see chapter 5.1.1: Turbidity, page 78.

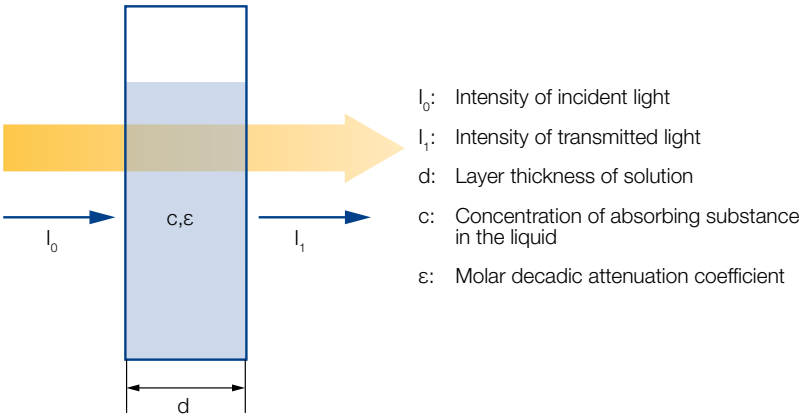

Figure 6: Light path in the measurement cuvette

1.2.1 Why is UV/VIS radiation being used?

Numerous inorganic and organic compounds absorb light especially in the ultraviolet and visible range. Some chemical compounds can be analyzed directly by photometry, while others must first be converted into suitable compounds, e.g. into a colored complex which concentration can then be measured.

In this context, luminous flux or radiant power refers to the amount of light passing through the cuvette within a defined time. Its unit is lumen or watt.

In summary it can be said that every substance has a specific absorption spectrum. Hereby, the plot of absorbance versus wavelength is used in photometry to determine concentrations. This is possible because absorbance is dependent on concentration.

E = Absorbance
λ = Wavelength [nm]

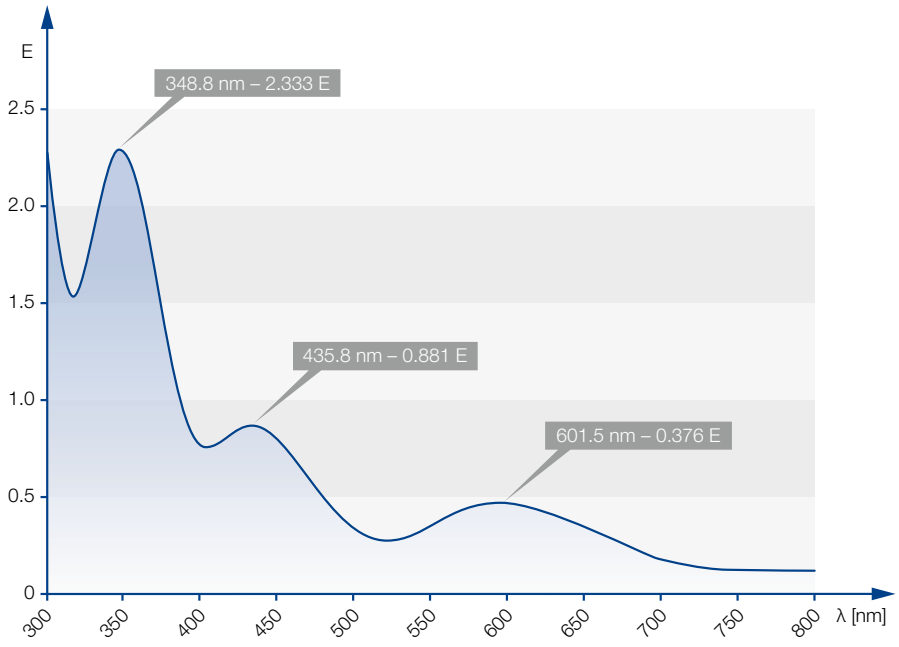

Figure 7: Spectrum of a COD test

Absorption spectra exhibit various forms, which can affect the measurement in different ways:

In the case of a sharp, steep-edged curve, even slight changes in wavelength results in higher deviations compared to curves that exhibit a broad maximum (e.g. in molybdenum blue solutions between 560–800 nm). Several maxima may occur within one spectrum at the same time (e.g. in silica: maxima at 360, 470, 570 nm), as well as maxima with a high or low intensity maximum.

The exact relationships are explained in the following section 1.3: Lambert-Beer Law.

1.3 Lambert-Beer law

The Lambert-Beer law (also known as Beer's law, the Beer-Lambert law, or the Beer-Lambert-Bouguer law) proves a relationship between concentration c, layer thickness d of the absorbing solution and absorbance E.

The relative decrease in intensity I is proportional to the layer thickness d. At the same time, the relative decrease in intensity is proportional to the concentration c of the dissolved absorbing substance as well.

Transmission is described as transmittance (T) and is the proportion of transmitted intensity of the incident light. Transmittance may be any value from 0 to 1.

$$T = \frac{I_1}{I_0}$$

The non-transmitted portion of the incident intensity is absorbed. The absorbed fraction (A) of the incident radiation is defined as follows.

$$A = 1 - T$$

Absorbance (E) is defined as the negative decadic logarithm of transmittance.

$$E = -\log T = -\log \frac{I_1}{I_0}$$

As mentioned previously, Lambert and Beer discovered the coherence between absorbance, concentration and layer thickness of a dissolved substance. Concentration is proportional to absorbance. The proportionality factor (ε) is the molar (spectral) absorption coefficient indicated as $L^{*}mol^{-1}cm^{-1}$. This is often referred to as the molar, decadic absorbance coefficient. Strictly speaking, this term is identical only in the absence of scattering.

The coefficient is temperature- and wavelength-dependent. The unit of concentration is $mol^{*}L^{-1}$, the layer thickness is given in cm. Accordingly, absorbance is a dimensionless quantity.

$$E = \varepsilon \cdot c \cdot d$$

$$c = \frac{E}{\varepsilon d} = F \cdot E$$

To determine the concentration of dissolved solids in the sample, this equation must be resolved to calculate the concentration. The resulting factor 1/εd is simplified as F.

The Lambert-Beer law proves a relationship between concentration, layer thickness of the absorbing solution and absorbance.

T = Transmittance
I_0 = Intensity of incident light
I_1 = Intensity of transmitted light
A = Absorption
E = Absorbance
ε = Molar decadic extinction coefficient
c = Concentration
d = Thickness of the solution layer
F = factor

Since the intensity of the light beam passing through the sample medium changes exponentially with concentration and layer thickness, plotting of concentration versus absorbance yields linearization. However, it is obvious that in the upper and lower limit area this curve shows some rounding. Here non-linearity is given and the measurements are distorted. Therefore, it is important to always work in the appropriate absorbance range. The optimum absorbance range is 0.1–1.0; here the error is less than one percent.

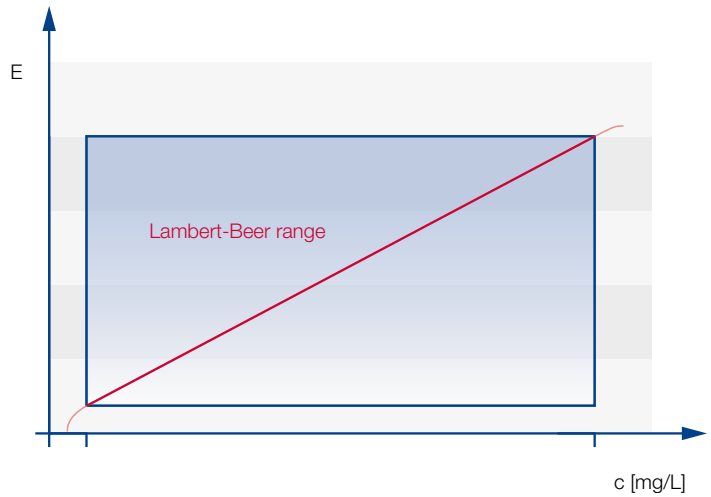

Figure 8: Diagram for the Lambert-Beer law

E = Absorbance
c = Concentration [mg/L]

Plotting of transmittance versus concentration would result in a curve with negative slope instead.

Most methods follow the Lambert-Beer law with a linear measuring range. The color intensity of the sample solution increases proportionally with absorbance.

E = Absorbance
c = Concentration [mg/L]
N = Zero value

$$m = \text{Slope} = \frac{\Delta_E}{\Delta_c} = \varepsilon d$$

$$\text{Factor } F = \frac{1}{m} = \frac{1}{\varepsilon d}$$

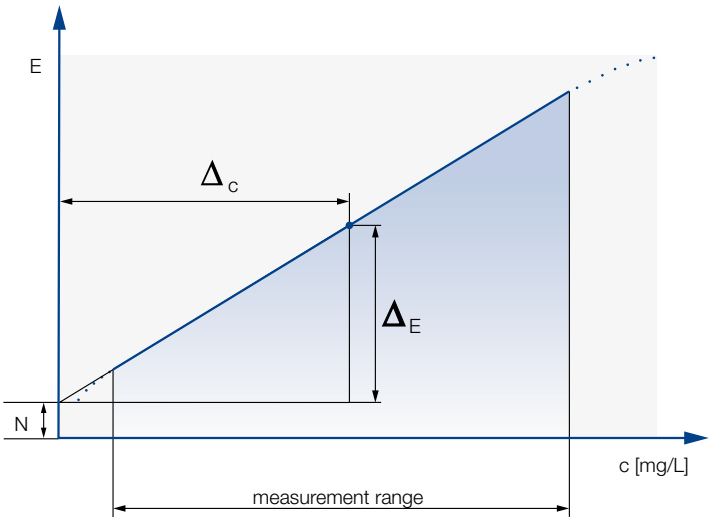

Figure 9: Methods with linear course

In a few tests (e.g. *NANOCOLOR*® COD tests with small measurement ranges, such as the *NANOCOLOR*® COD 60), the decrease in color intensity is measured.

However, there are also measuring methods in which linearity is not achieved. The factor then varies with concentration. This dependence is reproducible.

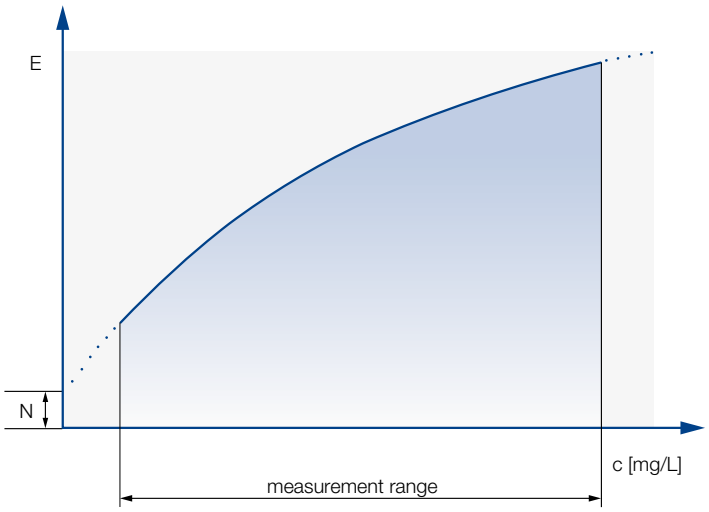

Figure 10: Methods with non-linear course

E = Absorbance
c = Concentration [mg/L]
N = Zero value

This non-linear curve can be assigned to optical as well as chemical causes.

Other sources of error are inherent in the Lambert-Beer law itself. The Lambert-Beer law requires a homogeneous absorbing substance of low concentration and negligible multiple scattering, no variation of the absorption coefficient within the measured irradiation area and no intrinsic emission. Concentrations that are too high might lead to interactions, distorting the measurement result.

Ideally, a solvent that has no inherent absorption is used and thus does not affect the measurement result. Furthermore, light of a fixed wavelength is required, so-called monochromatic light. The cuvette material affects the measurement results mainly in the UV range. Different compositions may lead to different results of the measurement.

Generally, a longer wavelength is advantageous in photometry, due to the lower sensitivity regarding impurities, low intrinsic color or reflection of the cuvette.

The absorbance can be influenced by the selection of different cuvette sizes and the dilution of the sample, i.e. concentration. Therefore, the measurement can be adjusted ideally.

1.4 Design of a photometer

1.4.1 The beam path inside a photometer

Each photometer comprises the following components: A radiation source, a device to produce collimated, monochromatic light (e.g. a filter), a sample compartment with cuvette and sample solution, a radiation receiver and an amplifier / display unit.

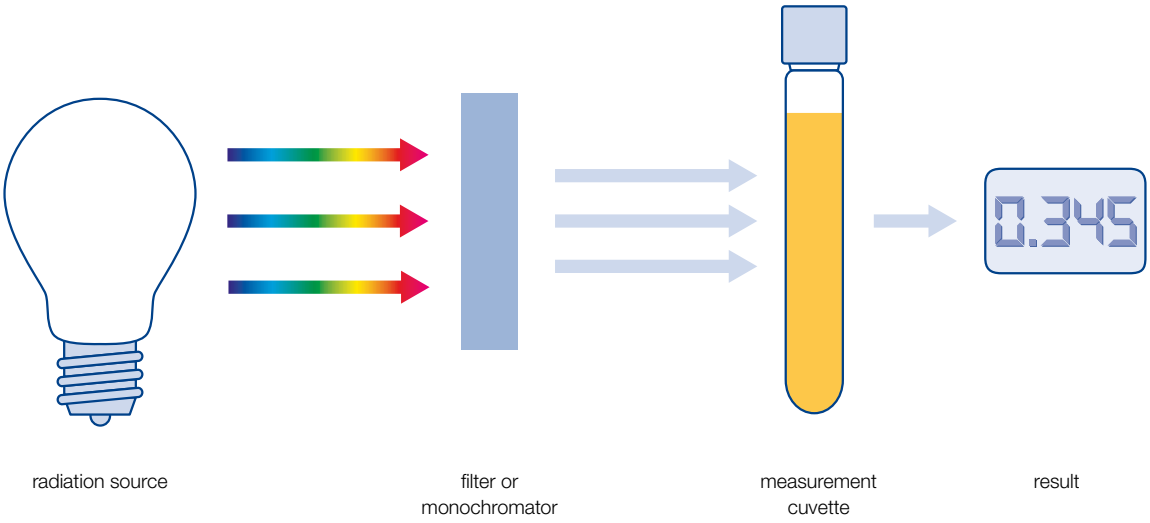

Figure 11: Schematic design of a single-beam photometer

Originating from a radiation source (tungsten halogen lamp or deuterium lamp in the *NANOCOLOR*® photometers), the emitted polychromatic light is focused on the sample compartment by an optical element (lens). Every colored substance absorbs only light of a specific wavelength, resulting from its spectrum. Therefore, monochromatic light (light of a specific wavelength) is required for the determination of the concentration of a colored solution. Two types of photometers can be distinguished:

Filter photometers and spectrophotometers

In filter photometers, monochromatic light is produced by using special interference filters for “filtering out” unwanted wavelengths. In a spectrophotometer, by contrast, the required wavelength is produced by a monochromator. This optical unit in the photometer generates monochromatic light by reflection of the beam path on a grid. Only the resulting, limited light beam is used for photometric evaluation.

When the light passes through the cuvette and sample solution, attenuation of the incident light occurs. The attenuated light beam which has passed the cuvette (transmission beam) impacts on the radiation detector which is located behind the sample compartment. A suitable photo-sensible element converts it into a digital measurement signal, which is ultimately shown on the display.

1.4.2 Filter photometer

In filter photometers, interference filters are used to select the optimum wavelength for the respective measurement. The selection of the correct filter depends on the color of the sample solution and the associated absorption of the complementary color. For a blue solution, a yellow filter is applied, while for a yellow solution a blue filter is used, since always the complementary color is absorbed.

Interference filters are glass panes that are usually coated with several semi-transparent dielectric layers. These special filter can be passed by discrete optical electromagnetic waves (light of certain wavelength), while others are reflected. This selectivity is based on the interference between directly incident and multiply reflected light. Interference is the superposition of one or several waves, which may lead either to their amplification or to their extinction.

It is important that the used filters let pass light of the correct wavelength (absorption maximum). The more closely the absorption maximum of the substance to be detected is approached, the higher the performance of the filter photometer will be.

Another important factor is bandwidth. Generally, bandwidth is the distance between an upper and lower limiting frequency. In photometry, bandwidth is the range between a lower and an upper wavelength. The smaller the spectral bandwidth, the higher the resolution. According to Lambert-Beer, monochromatic light is needed, corresponding to light with precisely one wavelength without bandwidth. This, however, cannot be realized in practice. Ideally, the applied filters have a minimum bandwidth.

A drawback of filter photometers is the limited range of possible wavelengths. The more filters, the higher the number of possible wavelengths of the incident polychromatic light that can be selected. However, only those wavelengths are available that result from the filters. If the absorption maximum of the parameter is closely outside the wavelength of the filter, the measurement becomes less sensitive because the wavelength of choice cannot be achieved.

1.4.3 Spectrophotometer

In contrast to the situation in a filter photometer, the exact wavelength in a spectrophotometer is isolated from the incident polychromatic light by a monochromator. The monochromator is an optical component. With the help of a reflective grid, the polychromatic light is split. Through an aperture as narrow as possible, only a small wavelength range of the light is transmitted into the direction of the cuvette. The undesired wavelength portion is absorbed by this aperture.

A spectrophotometer allows the performance of a scan over the entire wavelength range. Thereby, an absorption spectrum of the substance can be measured. Absorption maxima are directly detected. In addition, any wavelength of the incident light can be selected during the measurement. In contrast to filter photometers, after adjustment no deviation between the maximum of the absorption spectrum and the set wavelength is present. The measurements are more sensitive.

1.4.4 Cuvette

The selection of an appropriate cuvette for each measurement is crucial. The material (depending on the wavelength) and size of the cuvette are the two key factors.

By default, glass cuvettes are used, like those which are used for the *NANOCOLOR*® tube tests. The round cuvettes are so-called disposable cuvettes. They are discarded after single use. High-quality materials such as quartz are used in rectangular standard cuvettes for measurements in the UV range. In addition to round and rectangular cuvettes, there are also special cuvettes, such as flow-through cuvettes, where the sample solution is passed into and out of the cuvette by a pump.

The size of the cuvette is directly related to the layer thickness that is effective in the Lambert-Beer law. Generally speaking, the larger the cuvette and the sample volume, the greater the layer thickness, and the more sensitive the measurement can be. All *NANOCOLOR*® round cuvettes have an outer diameter of 16 mm (inner diameter and thickness = 14 mm), rectangular cuvettes are available in 10, 20 and 50 mm.

Cuvette test	Measurement range
NANOCOLOR® Cyanide 08 tube test	0.02–0.80 mg/L CN^-
NANOCOLOR® Cyanide standard test (50 mm)	0.001–0.50 mg/L CN^-

Table 3: The specified measurement range indicates the sensitivity of the relevant photometric test with different cuvette sizes.

A higher sensitivity, lowest measuring ranges and a maximum of measurement accuracy can be achieved with 50 mm rectangular cuvettes. Another advantage of standard tests is the variable measuring range due to the use of different cuvette sizes.

Figure 12: Various rectangular cuvettes

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2. Sampling, preservation and sample preparation

Correct sampling and sample preparation are extremely important for subsequent analysis. In order to get a correct result, a homogeneous and representative sample in compliance with any legal requirements and parameter-specific particularities has to be taken.

2.1 Sampling

There are various ways of sampling waste water, depending on the parameters to be examined. The goal is to take a representative sample.

Sample collection is the basic prerequisite for proper analytics. Errors made during the collection of a sample cannot be compensated in subsequent analysis. Such an error may amount to a whole order of magnitude. Especially in the analysis of very low concentrations, sampling is a crucial factor.

Before any sample is taken, the vessel should be rinsed (conditioned) several times with the sample solution.

Factors which might influence sample taking are listed in Figure 13.

Errors in sample taking cannot be compensated at a later stage of analysis.

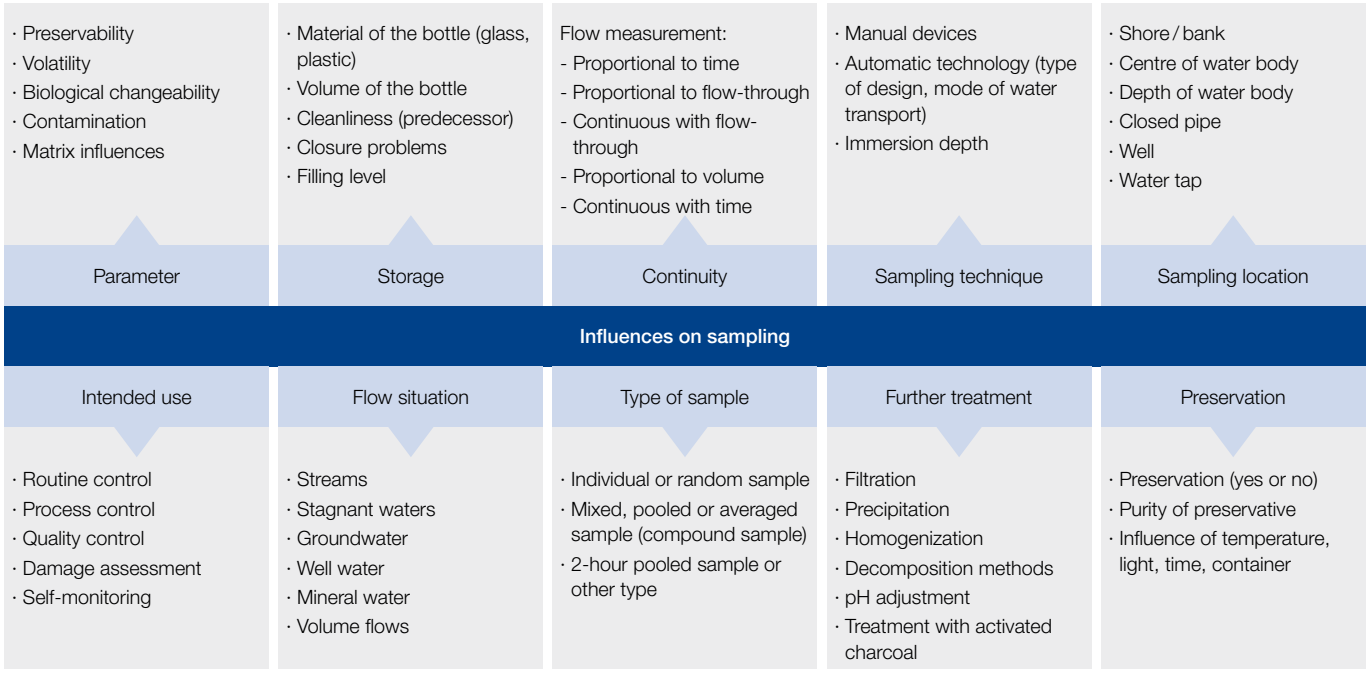
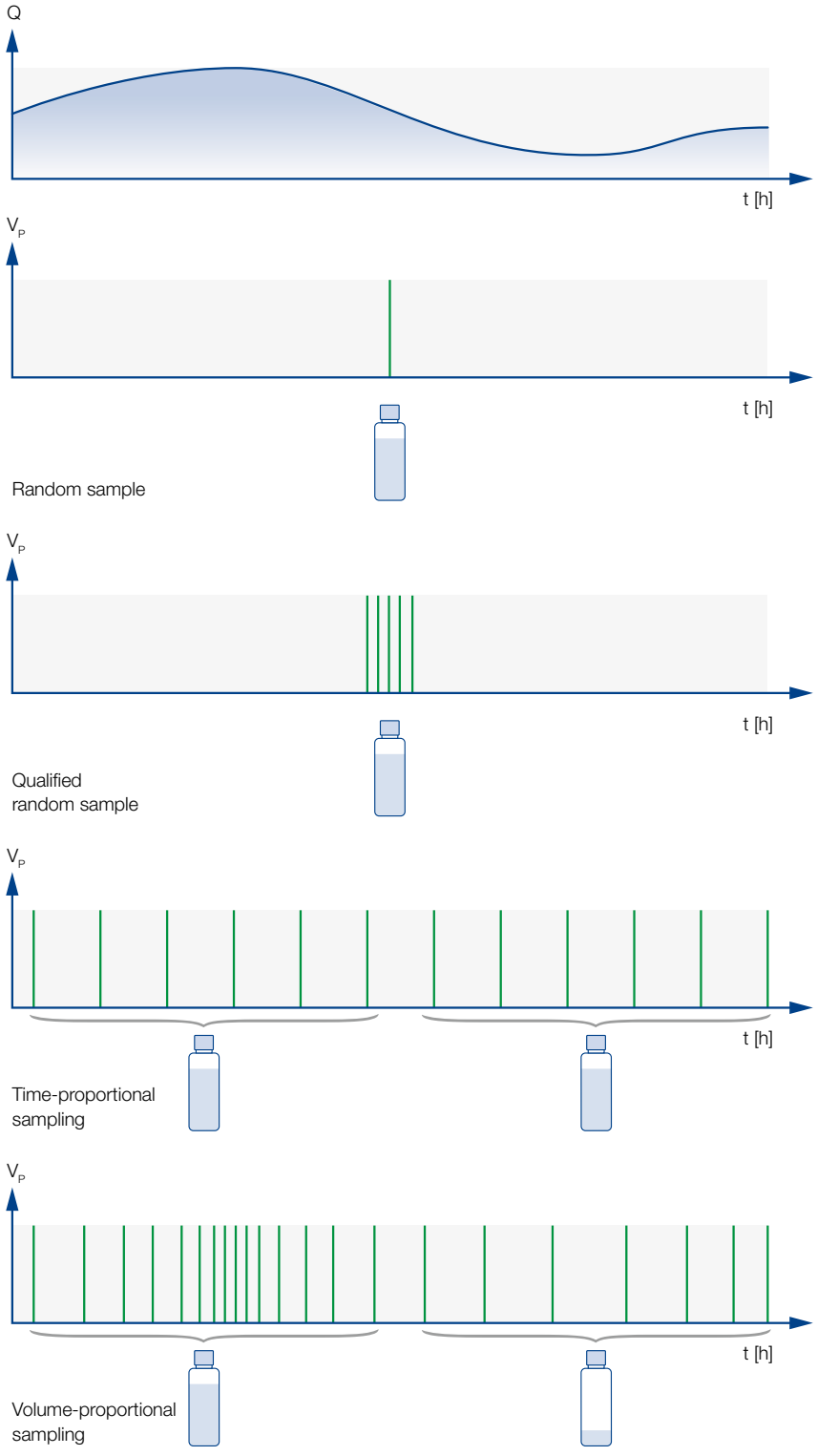


Figure 13: Influence of the individual analytic steps on the measurement result

Various modes of sampling are possible. Random samples, pooled samples, event-driven or various proportional samples can be taken. In wastewater treatment plants, population size plays a crucial role for the choice of the sampling method.

The meaning of the individual sampling processes is shown in the following illustrations.

Q = Quantity
t = Time [h]
= Sample quantity per bottle
V_P = Metering volume per sample



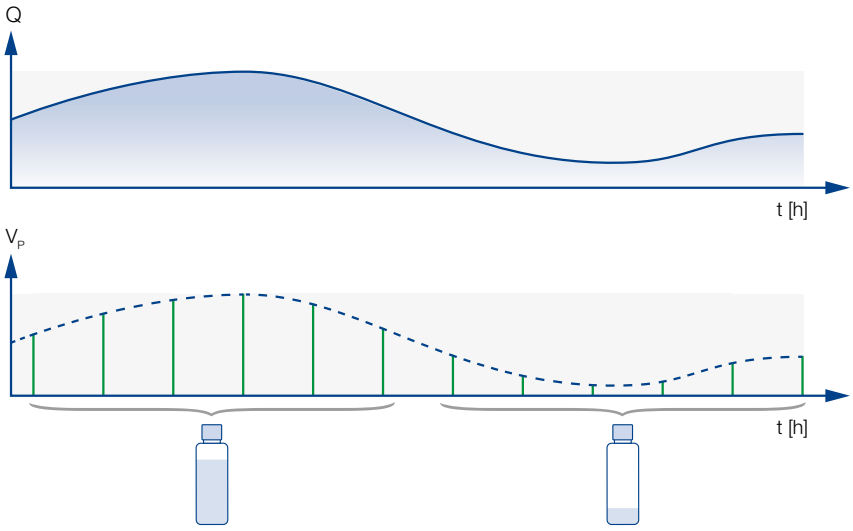
- One-time sampling
- At least 5 samples > 2 min for max. 2 h
- Regular time intervals
- Constant sample quantity
- Sampling by defined flow rate
- Constant sample quantity

Figure 14: Various sampling modes

A simple random sample is defined as the withdrawal of a single sample – or a plurality of single samples taken in immediate succession and combined to assess a current state. A qualified sample consists of at least 5 random samples taken at intervals of not less than 2 minutes during a maximum period of 2 hours.

The term pooled sample refers to two or more individually or continuously taken samples mixed at a suitable, known ratio to determine the average of a desired parameter from the mixture. An example for this is a 24-hour pooled sample (one-day pooled sample).

In time-proportional sampling, a constant quantity of sample is taken at regular time intervals. In volume-proportional sampling, the sampling depends on the defined flow rate. Here, too, always a constant quantity is removed.



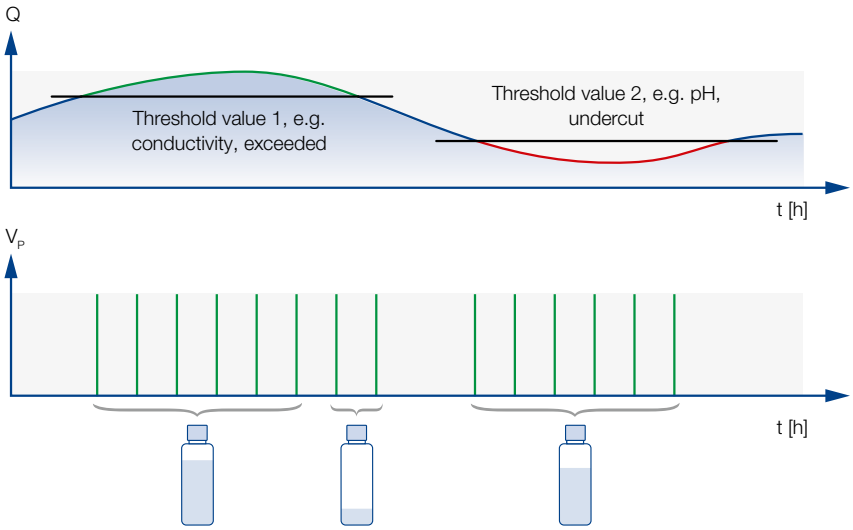
Q = Quantity
t = Time [h]
= Sample quantity per bottle
V_P = Metering volume per sample

- Regular time intervals
- Variable sample quantity

Figure 15: Flow-proportional sampling

Provided that the sampling is proportional to the flow, a sample of variable quantity is taken periodically (in accordance with the flow-through).

Sampling can also be event-driven. Herby, samples are taken after a specific event, such as a parameter rising above or falling below a threshold value.



Q = Quantity
t = Time [h]
= Sample quantity per bottle
V_P = Metering volume per sample

- Sampling in response to an event
- Constant sample size
- Constant frequency

Figure 16: Event-driven sampling

The taken sample should be transported in glass bottles or PVC containers. Water bearing large amounts of oil or pesticides requires the use of glass bottles.

Decanting into smaller containers or taking a partial sample initially requires re-homogenization, of the sample to remain representative. Homogenization can be accomplished by simply shaking and agitating. Further homogenization can be achieved using a mixer or Ultra-Turrax® directly before analysis.

Possible sources of error should be considered and excluded during sampling:

Error Sources					
Sampling	Preservation	Storage	Handling	Sample-specific	Sample preparation
· Incorrect sampling point · Contamination of sample by use of unsuitable sampling bottles · Loss of contents due to incorrect sampling technique, improper transport, air in the filled bottles · Accumulation of solids by rinsing with unsuitable rinse water (e.g. influent water)	· No or incorrect preservation of the sample (incorrect preservative, improper dosage or concentration of preservative) · Contamination of preservative	· Incorrect storage of sample (influence of temperature and of light)· · Incorrect sampling vessel (e.g. absorption of contents into/ release of substances from the vessel walls, insufficient sealing) · Too long storage before analysis	· Mix-up of sample due to illegible, absent or incorrect marking · Mix-up of bottle caps · Carryover of substances and contents due to insufficient rinsing and strong concentration differences (wastewater, potable water)	· Alteration of the sample by further chemical processes (e.g. oxidations or reductions) · Alteration of the sample by bacterial activity · Formation of precipitates · Loss of highly volatile substances by transport or movement	· Incorrect or no homogenization · No filtration for soluble compounds or filtration for cumulative parameters

Figure 17: Possible sources of error before photometric analysis

2.2 Preservation

It is not always possible to carry out the analysis immediately after sampling. Depending on the parameter, there are different means of sample stabilization (e.g. by adding acids or bases) and preservation. A proper preservation ensures that the sample will still be representative upon analysis.

Determination of the classic sewage parameter COD should always be conducted as soon as possible after sampling. If this is not possible, 1 liter of sample is adjusted to a pH value of 2 or lower with concentrated sulfuric acid. This acidified sample can be kept at room temperature for up to seven days. If the sample is stored at 4 °C, the analysis can be carried out up to 28 days after sampling. By cooling, biodegradation processes are slowed down. For metal parameters such as chromium, stabilization is carried out by the addition of nitric acid (HNO_3) to a pH of 1–2.

However, a few parameters, such as chlorine or oxygen, require direct analysis, due to preservation issues. Any delay will lead to incorrect measurement results.

By contrast, there are other parameters, e.g the concentration of chelating agents or chloride, that do not decompose over time but remain stable. Here the sample can be stored and analyzed later, even without special preservation.

High quality filter papers

MN filter papers since 1911

German Quality

- More than 7000 different filtration products
- Reliable results
- Flexible and custom-made products
- Special filter paper for sewage plants according to DIN EN 872

Table 4 gives an overview of the individual parameter-dependent preservation steps.

Parameter	Preservation
Acidity	Cool to 1–5 °C, 1 day
Alkalinity	Cool to 1–5 °C, 1 day
Aluminum	pH 1–2, HNO_3, max. 1 month
Ammonium	pH 1–2, H_2SO_4, max. 7 days
Anionic surfactants	Add of 1 % (v/v) of a 40 % formaldehyde solution, max. 4 days
AOX	pH 1–2, HNO_3, max. 1 month
BOD_5	Cool to 1–5 °C, 1 day
Bromide	Not required
Cadmium	pH 1–2, HNO_3, max. 1 month
Calcium	pH 1–2, HNO_3, max. 1 month
Carbonate hardness	Measure quickly, max. 1 day
Cationic surfactants	Measure quickly, max. 1 day
Chlorate	pH 10 ± 0.5, NaOH
Chloride	Not required
Chlorine	Measure immediately!
Chlorine dioxide	Measure immediately!
Chlorite	pH 10 ± 0.5, NaOH
Chromate	Cool to 1–5 °C, 1 day
Chromium	pH 1–2, HNO_3, max. 1 month
Cobalt	pH 1–2, HNO_3, max. 1 month
COD / TOC	pH 1–2, H_2SO_4, max. 7 days
Coloration	Measure quickly, max. 1 day
Complexing agents	Not required
Copper	pH 1–2, HNO_3, max. 1 month
DEHA (diethylhydroxylamine)	Measure immediately!
Dissolved silicate	Measure immediately!
Easily released cyanide	pH > 12, NaOH, max. 7 days
Ethanol	Cool to 1–5 °C, 1 day
Fluoride	Not required
Formaldehyde	Measure quickly, max. 1 day
Hardness	pH 1–2, HNO_3, max. 1 month
Hydrazine	Acidification with HCl to pH =1, dark, airtight, max. 1 day
Hydrocarbons	pH 1–2, H_2SO_4, max. 7 days
Hydrogen sulfide	Measure immediately!
Iron	pH 1–2, HNO_3, max. 1 month
Iron(II)	pH 1–2, HCl, max. 7 days
Lead	pH 1–2, HNO_3, max. 1 month
Magnesium	pH 1–2, HNO_3, max. 1 month
Manganese	pH 1–2, HNO_3, max. 1 month
Methanol	Cool to 1–5 °C, 1 day
Nickel	pH 1–2, HNO_3, max. 1 month
Nitrate	pH 1–2, H_2SO_4, max. 7 days
Nitrite	Measure quickly, max. 1 day
Non-ionic surfactants	Add of 1 % (v/v) of a 40 % formaldehyde solution, max. 4 days
Organic acids	Measure quickly, max. 1 day
Ortho-phosphate	pH 1–2, H_2SO_4, max. 7 days

Parameter	Preservation
Oxygen	Measure immediately!
Ozone	Measure immediately!
Peroxide	Measure immediately!
pH	Measure quickly, max. 1 day
Phenol index	pH < 4, H_3PO_4, dark, max. 21 days
Phenols	pH < 4, H_3PO_4, dark, max. 21 days
POC	Not required
Potassium	pH 1–2, HNO_3, max. 1 month
Silicic acid	Cool to 1–5 °C, 1 day
Silver	pH 1–2, HNO_3, max. 1 month
Starch	Measure quickly, max. 1 day
Sulfate	Cool to 1–5 °C, 1 day
Sulfide	Fixation of sulfide by adding 2 mL of zinc acetate solution (2 N) to 1 L sample solution, addition of NaOH if pH is not between 8.5–9.0, max. 7 days
Sulfite	Measure quickly, max. 1 day
Thiocyanate	Measure quickly, max. 1 day
Tin	pH 1–2, HCl, max. 7 days
Total cyanide	pH > 12, NaOH, max. 7 days
Total nitrogen	pH 1–2, H_2SO_4, max. 7 days
Total phosphorus	pH 1–2, H_2SO_4, max. 7 days
TTC	Measure immediately!
Zinc	pH 1–2, HNO_3, max. 1 month

Table 4: Parameter-specific sample preservation

2.3 Sample preparation

The sample solution should ideally be clear and colorless, free of interfering ions and turbidity in order to ensure error-free analysis. Additionally, each test requires a certain pH range in which it operates reliably. Therefore, samples often cannot be used directly, but need some preparation.

For cumulative parameters such as total phosphate, the homogenized sample is used directly for decomposition by oxidation. The sample may not be filtered, as complexed or poorly soluble phosphate compounds might be removed by filtration, which would result in lower apparent results. For further details on the decomposition process please refer to chapter 3: Decomposition Methods, page 27.

By contrast, the sample needs to be filtered if only ortho phosphate or other soluble compounds are to be analyzed, to remove any existing unwanted suspended solids and turbidity. Turbidity (opacity, clouding) is caused by small suspended (insoluble) particles which have a refractive index different from that of the medium. This results in absorption, scattering and reflection of the incident light, which in turn leads to incorrect results.

To remove finely dispersed turbidity, membrane filters with a small pore size (0.45 µm) are used. For the filtration of coarsely dispersed turbidity, qualitative paper filters are used (e.g. MN 615). Often an additional fine filtration by membrane filters is performed following the coarse filtration.

For cumulative parameters such as total phosphate, the homogenized sample is used directly for decomposition by oxidation. The sample must not be filtered.

Turbidity leads to increased absorption; therefore filtration is important for soluble compounds prior to analysis.

Reaction temperature and pH are important factors in analytics.

Cold or frozen samples must be warmed to room temperature (20–25 °C). All test kits are designed for usage at room temperature. If the sample is too cold, the reaction process may be impaired, and incorrect measurements may result.

The pH value is crucial for all chemical reactions. Some reactions occur only in acidic range, while others proceed at basic or neutral pH values. If the pH is too high or too low, it can be adjusted with acids or bases, respectively. The acids / bases must be suitable for the test. Any use of acids and bases is consequently a dilution of the parameter and thus has to be considered in the evaluation.

Example: Many tests are disturbed by chloride ions. Adjustment of the pH with hydrochloric acid is, therefore, inappropriate.

The required reaction temperature and the ideal pH of the sample solution are given in the respective instruction leaflets.

3. Decomposition procedures

In practice, analysis often detects only the dissolved portion of the substances of interest. Poorly soluble, polymeric or complex-bound substances, but also ions in other oxidation states than those accessible to the test, are not covered. Especially in heavily contaminated samples, the compounds are often present in a complexed form or otherwise bound.

Therefore, determination of a total amount of one compound implies decomposition prior to the measurement.

Decomposition converts poorly soluble compounds into readily soluble, analytically accessible ones.

Decomposition is a preparatory operation that is part of the sample preparation process. During decomposition, these substances are converted into readily soluble (water- or acid-soluble) compounds exploiting decomposition reagents. They become accessible to analysis. Interfering organic components are destroyed by decomposition, insoluble oxides (metal oxides) are dissolved, metal ions are extracted from complexes, and adsorptive compounds are eliminated.

Ideally, after decomposition the solution is clear and free of turbidity. If this is not the case a second decomposition with repeated addition of the decomposition reagent has to be performed. An insoluble sediment is allowed to settle, and only the supernatant is used for further analysis.

Depending on the parameters and substance to be analyzed, there are different decomposition methods. It is important to maintain the predetermined decomposition temperature and time. In case of failure to comply, it may happen that a certain proportion of poorly soluble compounds has not yet been converted into soluble compounds, which might lead to lower apparent results of the analysis.

3.1 When is decomposition required?

Generally, decomposition is mandatory whenever it is indicated in the instruction manuals, for example in the determination of COD, total nitrogen or TOC. In the determination of all so-called cumulative parameters, decomposition precedes analysis.

In the determination of cumulative parameters, decomposition is always required.

In addition, decomposition should be performed if there is evidence for the presence of chelating agents or other poorly soluble compounds which might otherwise not be analyzed. In case of uncertainty, the sample should be checked concerning these parameters prior to analysis. This can be done for example with the tube test for organic complexing agents.

In many tube tests, the required decomposition reagent is already included in the test (e.g. for COD, total nitrogen, total phosphate, total chromium). In other tests (e.g. for most metal parameters), the decomposition reagent is added additionally prior to conducting the test.

3.2 Decomposition reagents in photometric analysis

The performance of the decomposition mainly depends on the parameter to be determined, the chemical compounds present, and the concentrations in which the latter are present. In addition, factors such as sample quantity, subsequent analysis and possible matrix interferences play a role.

In most decompositions, peroxodisulfate is used as decomposition reagent. The advantages of peroxodisulfate are its high oxidizing power and the comparatively simple handling as a solid. During the decomposition process, peroxodisulfate is reduced to sulfate, while the compounds are degraded by oxidation.

Peroxodisulfates are among the strongest oxidizing agents known.

Figure 18 provides an overview of the individual decompositions that are important in photometric water analysis.

Decompositions for photometric analysis					
Decomposition with peroxodisulfate				Decomposition with potassium dichromate and sulfuric acid	Aqua regia decomposition with hydrochloric acid and nitric acid
Already integrated into test performance: · AOX · Total chromium · Total phosphate · Total nitrogen · TOC	*NANOCOLOR*® *NanOx* N: · Nitrate	*NANOCOLOR*® *NanOx* Metall: · Aluminium · Cadmium · Chromate · Iron · Cobalt · Copper · Nickel · Phosphate · Zinc	*NANOCOLOR*® Crack-Set: · Lead · Cadmium · Iron · Copper · Cobalt · Nickel · Zinc	Already integrated into test performance: · COD · Hydrocarbons	*NANOCOLOR*® Sludge: · Cadmium · Chromium · Copper · Nickel · Zinc

Figure 18: Overview of decompositions for photometric analyses

3.3 Determination of total nitrogen with *NANOCOLOR*® *NanOx* N

Initial decomposition is necessary for the determination of total nitrogen. Only a decomposition ensures that all nitrogen compounds present in the sample solution are detected in subsequent analysis.

Figure 19: Decomposition reagent *NANOCOLOR*® *NanOx* N (REF 918 979)

Peroxodisulfate oxidizes all nitrogen compounds to nitrate.

3.3.1 Principles of decomposition

The principle of this decomposition is the thermally induced oxidation of all organic and inorganic nitrogen-containing substances to nitrate (NO_3^-) by potassium peroxodisulfate. Decomposition takes place in a heating block (30 min at 120 °C). Alternatively, a microwave oven can be used for decomposition.

Residues of peroxide remaining after oxidation as well as any contained chromium(VI), which would interfere with nitrate determination, are eliminated by the compensation agent.

After decomposition, the determination is performed as nitrate-nitrogen using *NANOCOLOR*® Nitrate 50 (Test 0–64). The tests *NANOCOLOR*® total Nitrogen TN_b comprise the decomposition reagent *NANOCOLOR*® *NanOx* N and a corresponding test *NANOCOLOR*® Nitrate for subsequent analysis in one package.

3.3.2 Hints for sample solution

Prior to decomposition, the solution should be homogenized to obtain a representative sample.

The pH value of the sample to be decomposed must be between 5 and 9. Deviating values must be adjusted with sodium hydroxide or sulfuric acid. Nitrogen concentrations which are twice as high as the maximal measuring range can simulate proper values within the measuring range and thus can be misinterpreted.

The expected concentration of the sample must be previously diluted into the range specified by the test. Water of unknown concentrations require a plausibility check including significantly different dilutions (1+9; 1+99) until the last dilution confirms the value previously found.

Decomposition in a heating block at 120 °C has a lower oxidation potential than microwave decomposition. For primarily municipal waste waters, this method can be used if the matrix remains unchanged over longer periods. However, the results should be verified with comparative methods (e.g. microwave decomposition) regularly.

Compounds which are (virtually) inert to oxidation using peroxodisulfate might be detected only partially or even not at all. Incomplete decomposition can also be expected with samples consuming large amounts of oxidizing agents (e.g. samples with COD > 1000 mg/L O_2).

The inorganic components ammonium, nitrite and nitrate are included in the measured value along with other nitrogenous compounds such as amino acids, urea, complexing substances, etc.

The pH of the sample must be between 5 and 9.

Nitrogen concentrations twice as high as the double measuring range can simulate wrong measurement values.

3.3.3 Performance

Pipette 5.0 mL of the sample solution into a clean empty tube cuvette with OD = 16 mm (REF 916 80), add 1 orange measuring spoon full of *NANOCOLOR*® *NanOx* N decomposition reagent, close and shake thoroughly. Insert the round cuvette into a *NANOCOLOR*® heating block and heat for 30 min to 120 °C. Withdraw the reaction tube, invert briefly and allow to cool.

Open the reaction tube, add one measuring spoon of *NANOCOLOR*® *NanOx* compensation agent, close the round cuvette and shake vigorously once more.

The content can now be used as sample solution for the determination of total nitrogen TN_b using test 0-64 *NANOCOLOR*® Nitrate 50.

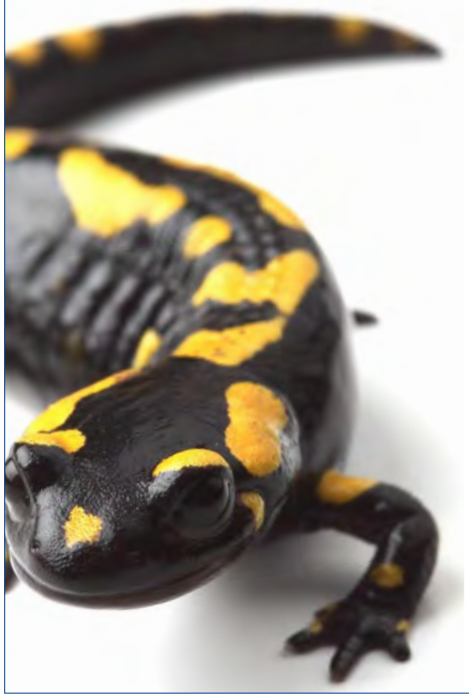
The leaflet of *NANOCOLOR*® *NanOx* N can be downloaded for free from ***www.mn-net.com***.

NANOCOLOR® VARIO 4 and *VARIO C2*

Heating blocks of the future

Experience flexibility

- Touch screen with intuitive user guidance
- Extremely short warm-up times and high temperature stability
- Internal quality control according to ISO 9001
- COD, total-N and total-P in just 30 minutes



3.4 Determination of total metal and total phosphorus with *NANOCOLOR*® *NanOx* Metal

For determination of total metal or total phosphorus, initial decomposition is necessary. That all metal or phosphorus compounds present in the sample solution are detected in subsequent analysis can only be ensured by decomposition.

Figure 20: Decomposition reagent *NANOCOLOR*® *NanOx* Metal (REF 918 978)

3.4.1 Principles of decomposition

The principle of oxidative decomposition is the detection of total phosphorus and complexed metals or metal ions present in an oxidation state in which they would escape detection without decomposition. The decomposition is carried out under heating with sodium peroxodisulfate in a heating block or alternatively in a microwave oven.

After decomposition, the neutralization reagent (sodium hydrogen carbonate) is added to adjust the pH.

Peroxodisulfate oxidizes all phosphorus compounds to phosphate and all metal compounds to higher, analyzable oxidation states.

3.4.2 Hints for sample solution

The sample should be homogenized prior to decomposition to obtain a representative sample.

The expected concentration of the sample must previously be diluted into the range specified by the test. Water of unknown concentrations require a plausibility check including significantly different dilutions (1+9; 1+99) until the last dilution confirms the value previously found.

NANOCOLOR® *NanOx* Metal is suitable for decomposition in a heating block at 100/120 °C and in a microwave oven. Decomposition in a heating block at 100/120 °C has a lower oxidation potential than microwave decomposition and should be verified by dilutions and comparison with microwave decomposition. Compounds which are (virtually) inert to oxidation using peroxodisulfate might be detected only partially or even not at all. Incomplete decomposition can also be expected with samples consuming large amounts of oxidizing agents (e.g. samples with COD > 1000 mg/L O_2).

For test solutions with unknown concentrations of metal or phosphorus compounds, or samples which are expected to have a high oxidant consumption, it is recommended to prepare several samples with different dilutions (e.g. 1+1, 1+9) to confirm the obtained analysis value. The dilution must be accounted for in the measured value.

The package insert of *NANOCOLOR*® *NanOx* Metal can be downloaded for free from ***www.mn-net.com*** .

3.4.3 Performance

Pipette 6.0 mL of the sample solution into an empty round cuvette with OD = 16 mm (REF 916 80), add 1 orange measuring spoon full of *NANOCOLOR*® *NanOx* Metal decomposition reagent, close and shake thoroughly. Insert the round cuvette into the heating block and heat to 100 °C for 1 hour or for 30 min to 120 °C. Remove the round cuvette from the heating block, allow to cool and invert briefly.

The decomposition solution must be clear and colorless. Otherwise repeat the procedure. If insoluble sediments are present they are allowed to settle, and only the supernatant is used for further analysis.

Invert the reaction tube once and open it, test with QUANTOFIX® Peroxide 25 (REF 913 19) for absence of peroxides. If peroxides are still present, heat the decomposition solution once more without further addition of *NANOCOLOR*® *NanOx* Metal decomposition reagent.

If the decomposition solution is free of peroxides, carefully add 3 microspoons of *NANOCOLOR*® *NanOx* Metal neutralization reagent (caution: release of gas), close and shake vigorously once more. The pH must be 3–7, otherwise use more neutralization reagent.

The content can now be used as a sample solution for the mentioned phosphorus and metal determinations. Please note that in case of a modified sample volume the measurement results of the standard tests have to be multiplied by the appropriate dilution factor

XL decomposition permits determination of 4 metal tests per XL tube.

XL decomposition:

As an alternative to the normal decomposition, it is also possible to perform a XL decomposition. Instead of 6 mL sample solution, 17 mL sample solution per tube are decomposed. Please note that this decomposition requires larger tubes (REF 916 22) as well as a different heating block (REF 919 350.1).

This decomposition is ideal if several metal parameters are to be determined.

Required accessories:

Heating block *NANOCOLOR*® *VARIO C2* M (REF 919 350.1)

NANOCOLOR® decomposition tube OD = 22 mm (REF 916 22)

Pipette 17 mL of sample solution into an empty decomposition vessel (REF 916 22), add 3 orange measuring spoons of *NANOCOLOR*® Metal decomposition reagent, close and shake thoroughly. Insert the reaction tube into the heating block *NANOCOLOR*® *VARIO C2* M and heat for 30 min to 120 °C or for 1 h to 100 °C. Remove the vessel from the heating block, allow to cool and invert briefly.

The decomposition solution must be clear and colorless. Otherwise decompose once more. If any insoluble sediment is present it is allowed to settle, and only the supernatant is used for further analysis.

Invert the reaction tube once and reopen it, test with QUANTOFIX® Peroxide 25 (REF 913 19) for the absence of peroxides. If there should still be peroxides, heat the decomposition solution once more without further addition of *NANOCOLOR*® *NanOx* Metal decomposition reagent.

If the decomposition solution is free of peroxides, carefully add 3 black metal measuring spoons of *NANOCOLOR*® *NanOx* Metal neutralization reagent (caution: release of gas, please pay attention to general notes on performance), close, and shake vigorously once more. The pH must be 3–7, otherwise use more neutralization reagent.

The content can now be used as sample solution for the mentioned phosphorus and metal determinations. Please note that in case of a modified sample volume the measurement results of the standard tests have to be multiplied by the appropriate dilution factor. After completion of the analysis, remove the decomposition solution from the decomposition vessel, clean the test tube with a bottle brush and rinse it with distilled water.

Hint for XL decomposition:
Using two large decomposition vessels, up to four further reaction tubes with OD = 16 mm can be inserted into the heating block!

3.4.4 Parameters

After decomposition with *NANOCOLOR*® *NanOx* Metal, various metal parameters can be determined. Not every parameter requires addition of the neutralizing agent after decomposition. The parameters that can be determined and the particularities that require care are listed in Figure 21.

Using two large decomposition vessels, up to four further reaction tubes with OD = 16 mm can be used.

The following determinations can be performed after decomposition with *NANOCOLOR*® *NanOx* Metal:

Normal performance	Modified Performance
· Test 0-98 Aluminium 07 [a]	· Test 0-24 Chromate 5 (Chromium) [b]
· Test 1-02 Aluminum [a]	· Test 1-25 Chromate (Chromium) [b]
· Test 0-14 Cadmium 2	· Test 1-36 Iron [b]
· Test 1-51 Cobalt	· Test 0-37 Iron 3 [b]
· Test 0-61 Nickel 7	· Test 1-53 Copper [c]
· Test 0-71 Nickel 4	· Test 0-54 Copper 7 [d]
· Test 1-62 Nickel	· Test 0-53 Copper 5
· Test 0-76 Phosphate 1 (Phosphorus)	· Test 0-79 Phosphate 50 (Phosphorus) [b]
· Test 0-81 Phosphate 5 (Phosphorus)	
· Test 0-80 Phosphate 15 (Phosphorus)	
· Test 0-55 Phosphate 45 (Phosphorus)	
· Test 1-95 Zinc	
· Test 0-96 Zinc 4	

[a] Can be performed only in the microwave oven.
[b] Step 2 “Addition of the *NANOCOLOR*® *NanOx* Neutralization Reagent” can be waived.
[c] Instead of the neutralization reagent, use the double quantity of reagent R1.
[d] Instead of the neutralization reagent, use the double quantity of reagent R2.

Figure 21: Possible determinations after decomposition with *NANOCOLOR*® *NanOx* Metal

3.5 Tips & tricks

Homogenization

· Homogenization should be performed prior to decomposition in any case. Only thus, a representative sample and a meaningful analysis result can be obtained.

· The decomposition solution must be clear and colorless after decomposition. Otherwise repeat the procedure. Any insoluble sediment is allowed to settle, and only the supernatant is used for further analysis.

Neutralization

· After decomposition, the sample must be neutralized in a test-specific manner. Not all subsequent tests require neutralization., The respective pH range is indicated in the instruction leaflet. In tests that are performed in the acidic pH range (such as total chromium), neutralization is not required. More information can be found in the instruction leaflet of *NANOCOLOR*® *NanOx* Metal.

Need for decomposition

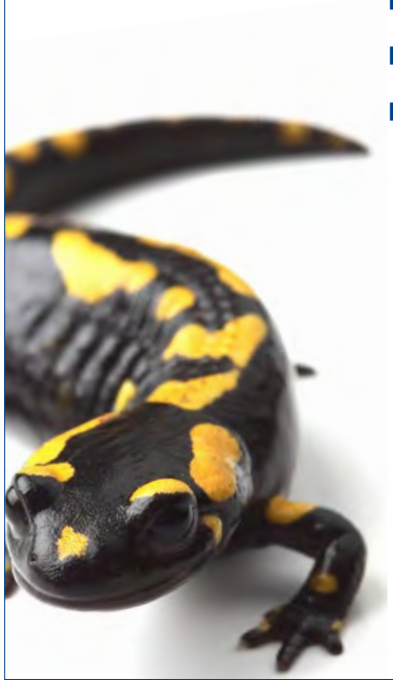
· Decomposition is required whenever determination of the total content of a compound is prescribed, e.g. by a regulation, or by an operating procedure (such as for COD or TOC). In addition, decomposition should be performed whenever chelating agents or poorly soluble compounds may be present in the sample.

Turbidity

· A turbid sample must not be filtered prior to decomposition. Filtration might remove poorly soluble compounds that are thus not decomposed and determined, which leads to lower apparent results.

NANOCOLOR® VARIO HC

The heating block with active rapid cooling



Heating and Cooling

- All important parameters in just 30 minutes
- Operation without time-consuming training
- Heating unit with aerator - Active rapid cooling after digestion

4. Important parameters in water and wastewater analysis

The quality of a water sample crucially depends on the quantity of certain chemical or biological parameters contained. The concentrations of entering parameters affect the water bodies. Some theoretical background knowledge is required for a better understanding of the analysis, the meaning of each parameter and the chemical relationships.

The most important parameters in water and wastewater analysis will be discussed in more detail in this chapter.

4.1 Sewage treatment plant parameters

The degree of contamination of waste waters in sewage treatment plants is defined by several parameters. The important cumulative parameters COD and total-N, as well as some individual parameters play a role.

Useful background knowledge, information on sample preparation and preservation and reaction basics for the main sewage treatment plant parameters are explained below.

4.1.1 Ammonium (NH_4^+)

Ammonium compounds are present in many surface waters and some groundwaters. Furthermore, they are always present in municipal and often in commercial and industrial wastewaters. There are various reasons for the presence of ammonium compounds in different types of water. They are e.g. products of chemical waste or they are bacterial degradation processes of nitrogen-containing organic compounds. The latter indicate pollution of the water with feces or other putrefaction and decay processes. Ammonium compounds enter our waters also with the rain, in the form of fertilizer ingredients being washed into the water. Almost all volcanic rocks In the mineral kingdom contain small quantities of ammonium salts.

The ammonium content in pure waters is less than 0.1 mg/L; special cases with levels up to 1 mg/L are swamp waters and special groundwaters with high iron and manganese contents (e.g. in the North German Plain). In polluted waters, concentrations up to 10 mg/L can be detected.

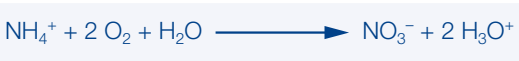
Toxicity in fish waters is mainly dependent on the pH of the water. Ammonium compounds are harmless at low pH values. However, with increasing pH an increasingly higher portion of fish-toxic ammonia is present. This can be explained from the following pH-dependent equilibrium between ammonium ions and ammonia:

Toxicity in fish waters is mainly dependent on the pH value of the water.

NH_4^+ = ammonium ion
OH^- = hydroxide ion
NH_3 = ammonia
H_2O = water
O_2 = oxygen
NO_3^- = nitrate ion
H_3O^+ = hydronium ion

At a pH of 6, the equilibrium is almost entirely on the left side, at a pH value of 8 already 4 % of ammonia, at pH 9 already 25 % and at pH 10 even 78 % of ammonia are present (at a water temperature of 17 °C). The level of toxicity depends on exposure time, temperature and fish species. On average, 1 mg/L NH_3 is reported as lethal to fish.

High ammonium concentrations also strongly decrease the oxygen concentration in water, since the bacterial oxidation of ammonium to nitrate (“nitrification”) consumes oxygen O_2:



Nitrification is essential for the natural purification process in water. But in case of high ammonium or ammonia content the nitrification leads to increased oxygen consumption and thus kills fish (for more information see 4.1.5: Nitrification, page 43).

The nitrification process is utilized in biological wastewater treatment plants for cleaning. Therefore, monitoring of the involved parameters ammonium, nitrite and nitrate plays an immense role. The ammonium concentration in the influent determines the oxygen demand in wastewater treatment plants. Thus the residual ammonium content in the plant effluent provides information on the effectiveness of the system.

Ammonia is cytotoxic to higher organisms. It is produced as a metabolic intermediate in the brain, the muscles, the liver, the intestine and the kidney. In the body, ammonia is immediately rendered harmless by the reaction with carbon dioxide to urea and the following conversion to glutamine. Unlike free ammonia, ammonium salts are non-toxic.

Ammonium salts are non-toxic, unlike free ammonia.

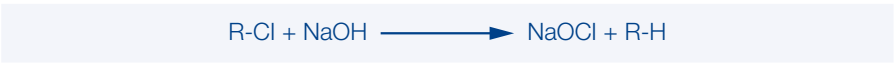
4.1.1.1 Reaction basis

Colorimetric and photometric determinations are performed in accordance to the Berthelot reaction (underlying reaction in analogy to ISO 7150-1, APHA 4500-NH_3-F, EPA 350.1 and DIN 38406-E5).

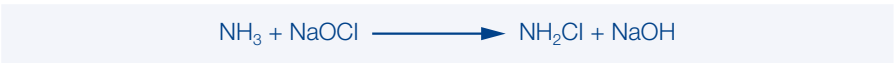
Ammonium or ammonia reacts with hypochlorite and salicylate in strongly alkaline solution (pH ≈ 12.6), in the presence of sodium nitroprusside (sodium (nitrosopentacyanoferrate(III)) as a catalyst to form a blue indophenol.

In the first reaction step, hypochlorite is generated in situ from dichloroisocyanuric acid in alkaline medium.

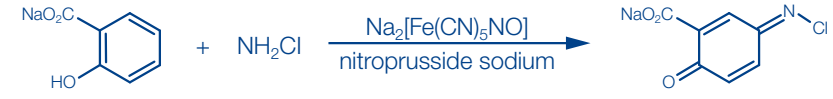
R-Cl = dichloroisocyanuric acid
R = generic residue
NaOH = sodium hydroxide
NaOCl = sodium hypochlorite
NH_3 = ammonia
NH_2Cl = chloramine



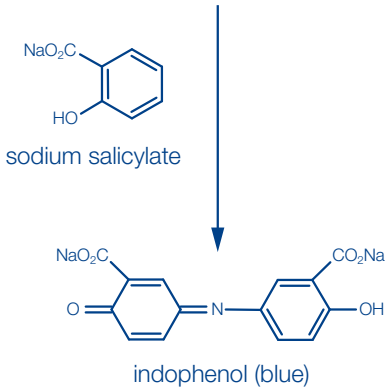
The hypochlorite reacts with ammonia to form chloramine.



With a catalytic amount of sodium nitroprusside, chloramines react with phenols (here: sodium salicylate) to form quinonimines. The quinonimine reacts with a further equivalent of sodium salicylate, resulting in a blue indophenol.



sodium salicylate chloramine quinonimine



sodium salicylate

indophenol (blue)

4.1.1.2 Sample preservation

· The sample can be stored for 7 days until the start of analysis, after stabilization of the pH with H_2SO_4 to pH 1–2 and filtration on site (storage vessel: PE or glass bottle).

4.1.1.3 Tips & tricks

Sea water suitability

· Almost all *VISOCOLOR*® and *NANOCOLOR*® ammonium tests are suitable for sea water analysis; some require dilution (1+1 or 1+9). For more information, please refer to the respective instruction leaflet.

pH

· The reaction solution or sample must not be too acidic. Strongly acidic and buffered samples must be adjusted to a pH in the required range before the test, using sodium hydroxide. Different pH values of the sample solution are required depending on test kit and measurement range. The exact specification can be found in the instruction leaflets.

· The ammonium nitrogen in water is present in the equilibrium NH_4^+ / NH_3 (NH_4OH) depending on the pH; both forms are completely detected by the analysis.

· The pH values for the sample solutions stated in the instruction leaflets must be complied with.

Reaction temperature

· The reaction temperature must be controlled, because the reaction time of 15 min applies only at T = 20 °C. Different temperatures may yield lower apparent results.

Interferences

- Primary amines react like ammonium ions and therefore lead to higher apparent results.
- Chlorine-consuming substances can lower the result or even inhibit the reaction, depending on concentration.
- Further interfering ions are listed in the instruction leaflets.
- Color formation is suppressed in case of highly concentrated samples (multiple concentration) of oxidizable substances, e.g. a high COD. In this case, the problem can be solved by dilution.

Performance of the test

- Do not leave the tube open for too long after the addition of reagent R2 to the *NANOCOLOR*® tube tests. Otherwise NH_3 gas will escape, leading to a risk of lower apparent results.
- Good reproducibility is achieved in weakly polluted waters. Heavy pollution causes errors and requires distillation prior to the analysis.

Turbidity

- Filter the sample in case of turbidity; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter papers (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber papers (e.g. MN 85/70 BF) or membrane filtration set GF / PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF / PET 0.45 µm.

4.1.2 Biochemical oxygen demand (BOD)

Besides the chemical oxygen demand (COD), the biochemical oxygen demand after 5 days (BOD_5) is the most important cumulative effect parameter for assessment of the degree of contamination of a water body.

The BOD is defined by the volume-related amount of oxygen which is consumed by micro-organisms to degrade the organic matter present in the water at 20 °C by oxidation. In general, this determination is made after 5 days, why it is often referred to the BOD_5 value.

The BOD provides information on the biologically utilizable portion of organic contents in the sample solution. The determination is made by the measurement of the consumption of oxygen required for the oxidative degradation. The information is indicated in mg/L O_2.

Alternatively, the carbon dioxide content can be measured instead of the oxygen content by so-called respirometric methods. Added sodium hydroxide reacts with the developing CO_2 gas to form sodium carbonate, which creates a negative pressure.

The more organic nutrients are present in the sample, the higher is the metabolic activity of the bacteria and hence the resulting BOD value. A statement about the quality of a water sample and its biological activity can be made based on the BOD value.

- A high BOD value corresponds to a high concentration of readily degradable organic substances.
- A low BOD value can be caused by a low concentration of biologically utilizable substances, by poorly degradable compounds or by a disturbed determination of the BOD value.

The BOD is often evaluated in the context of the COD. If the difference between the two values is small, the sample consists mostly of readily biodegradable substances. If the difference is, however, very large, this can be attributed to a poor bio-degradability.

Nitrogen degradation also takes place, in addition to carbon degradation, in the sample solution. Nitrogen degradation, also known as nitrification, is the conversion of ammonia into nitrate. This happens also under oxygen consumption. In general, nitrification occurs later than carbon degradation. Nitrification inhibitors are used in order to exclude any disturbance on the BOD that might nevertheless occur, especially in lightly contaminated samples. The most commonly used compound is *N*-allylthiourea (ATH or NATH).

At high BOD concentrations, the sample must be treated with dilution water. Dilution water is unchlorinated tap water aerated for at least one hour in the dark. The oxygen concentration of the dilution water should be at least 8 mg/L.

Oxygen determination of carbon degradation is disturbed by nitrogen degradation. As a preventive measure, nitrification inhibitors are used.

Inoculating water, which is aerated inoculated dilution water, must be used for dilution, if the sample was frozen or does not contain enough micro-organisms. Inoculating water is obtained from microorganism-rich water such as sedimented municipal wastewater from the runoff of the primary treatment or from the mechanical feed. More information can be found in the instruction leaflet of the BOD accessories set (REF 916 925).

4.1.2.1 Reaction basis

The BOD content is determined by measuring the oxygen concentration. Micro-organisms consume oxygen during the degradation of organic substances into carbon dioxide.

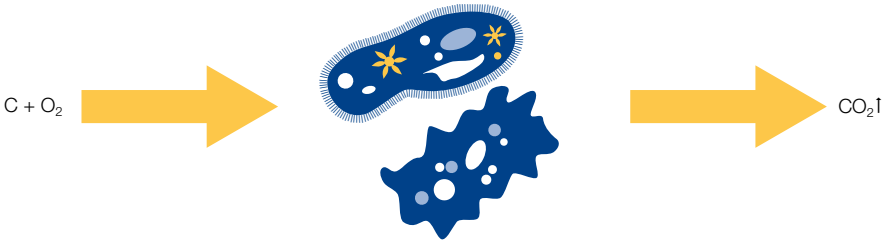


Figure 22: Principle of BOD determination

The simplified determination of the biochemical oxygen demand after 5 days (BOD_5) is done with undiluted samples and without using a control in accordance with the German norm DIN EN 1899-2-H52. The oxygen-enriched, undiluted sample is incubated in a test tube for 5 days at 20 ± 1 °C in the dark. The determination of the dissolved oxygen after 5 days is based on the Winkler method. The incubation of the sample and the oxygen measurement (after 5 days) take place in the same test tube (REF 985 825).

In the standard method, the BOD_5 is determined according to the so-called dilution principle. The oxygen concentration is measured immediately after sample preparation and after five days of incubation in Winkler bottles (REF 985 822). This method is in accordance with the German norm DIN EN 25813-G21.

4.1.2.2 Sample preservation

- Store the sample immediately after collection in a completely filled (no air bubbles!), tightly sealed bottle at a temperature of 1–5 °C in the dark until the performance of the test.
- Start the test as soon as possible, at the latest after 24 hours. Freeze the sample for longer storage.

4.1.2.3 Tips & tricks

The BOD test measures the decrease in oxygen.

Background information

- The test measures the oxygen consumption. A too high oxygen consumption of the dilution water leads to incorrect results. When using dilution water, measure the oxygen content of the control sample on day 0 (must be at least 8 mg/L O_2) and on day 5 before starting the measurements. If the oxygen concentration difference of the control sample is greater than 2 mg/L O_2, the oxygen degradation of the dilution water is too high. Possibly increase the aeration time or check for interfering ions.
- The same as described above applies when inoculating water is used instead of dilution water. The inoculating water must not have a high oxygen consumption. Again, oxygen measurements on day 0 and on day 5 before starting the analysis are recommended. The COD content of the inoculating water should be checked, if the oxygen consumption is too large. The COD content should be lower than 300 mg/L O_2. For higher COD concentrations, use less or if possible no inoculating water for the dilution water.

Sea water suitability

- Sea water analysis is possible.

pH

- The pH value must be between 6 and 8. pH values outside this range lead to incorrect results. If the pH is too high adjust with 0.1 N sodium hydroxide, if it is too low adjust with 0.1 N hydrochloric acid.

Interferences

- Accumulations of special microbial metabolites and substances toxic for micro-organisms (e.g. mycotoxins, free chlorine, certain heavy metals) can lead to reduction of the substrate conversion and thus to reduction of the BOD_5.
- Iron(II) salts, sulfur dioxide and hydrogen sulfide consume oxygen and also distort the BOD_5 test result.
- Presence of algae or nitrifying micro-organisms can lead to increased results.
- Free and / or bound chlorine has to be removed by adding a suitable amount of sodium sulfite.

4.1.3 Chemical oxygen demand (COD)

The chemical oxygen demand (COD) is one of the most important parameters for the assessment of industrial and municipal wastewater. As a cumulative parameter, COD determines all chemically oxidizable components present in water. Hence, this includes not only biodegradable substances (as in the BOD_5), but also chemical compounds that cannot be determined by biological oxidation (e.g. nitrogen compounds such as nitrites). It has also the advantage of a faster availability compared to BOD.

The COD covers all oxidizable contents of the sample.

The COD indicates the contamination of a water sample. It is therefore also used as an evaluation parameter to determine pollution units in discharges under the German Wastewater Charges Act.

By definition (ISO 15705), the COD is the concentration of oxygen that is equivalent to the mass of potassium dichromate that is consumed in total oxidation of organic substances present in the water sample. Mercury sulfate and silver sulfate as well as sulfuric acid are listed as auxiliary reagents.

COD is not a quantity-based size but an effect parameter (a requirement), as is illustrated in the following example:

$$K_2Cr_2O_7 + 8\ H^+ \longrightarrow 3\ <O> + 2\ Cr^{3+} + 2\ K^+ + 4\ H_2O$$

$K_2Cr_2O_7$ = potassium dichromate
H^+ = hydrogen ion
Cr^{3+} = Cr(III) ion
K^+ = potassium ion
<O> = Oxygen compounds
H_2O = water

In acid medium, potassium dichromate forms reactive oxygen species <O>, by the reaction with hydrogen ions.

$$CH_3OH + 3\ <O> \longrightarrow CO_2 + 2\ H_2O$$

These oxygen compounds are able to oxidize organic compounds such as ethanol or methanol to carbon dioxide.

$$CH_4 + 4\ <O> \longrightarrow CO_2 + 2\ H_2O$$

The consumption of oxidizing agent is independent of the size of the molecule. For example, the oxidation of methanol consumes less oxidant than that of the smaller methane, since less oxygen is consumed in the reaction to carbon dioxide and water. This results in a larger theoretical COD for methane than for methanol.

The COD content can be determined from the consumption of potassium dichromate. The evaluation is done photometrically or by titration.

In COD testing with a low measurement range, the decrease of the potassium dichromate concentration is determined; in COD tests with a higher measurement range, by contrast, the increase in Cr(III) ion concentration is determined.

Depending on the measurement range, the decrease in concentration of the yellow potassium dichromate or the increase in concentration of the green chromium(III) ion is determined. For all tests with a low measurement range, up to the test *NANOCOLOR*® COD 300 (REF 985 033), the former applies. From the test *NANOCOLOR*® COD 600 (REF 985 030) on, the increase of the green chromium(III) is determined.

An important process in COD determination is decomposition. In analogy to DIN 38409-H41, decomposition is carried out for two hours at 148 °C. A faster decomposition at 160 °C for 30 minutes is also possible. However, this rapid decomposition is not suitable for all tests. Please refer to the instruction leaflet of the respective test. COD decomposition in a microwave oven, in analogy to decompositions with *NANOCOLOR*® *NanOx* N and *NANOCOLOR*® *NanOx* Metal, is not permitted for safety reasons.

4.1.3.1 Reaction basis

The chemical oxygen demand of a water is determined by silver-catalyzed oxidation (increase in the oxidizability of aliphatic substances) with potassium dichromate / sulfuric acid for 2 hours at 148 °C. Possibly present chloride is precipitated by mercury sulfate

as undissociated mercury chloride. Thus it is removed from the unwanted oxidation to elemental chlorine. Silver sulfate serves as a catalyst to increase the oxidizability of aliphatic substances. Thus lower apparent findings are avoided.

The underlying reaction is analogous to APHA 5220-D, EPA 410.4 and DIN 38409-H41. Furthermore, seven *NANOCOLOR*® COD tests meet the requirements of the DIN ISO 15705:2002 standard.

Seven *NANOCOLOR*® COD tests meet the requirements of the standard ISO 15705:2002.

The main reaction is described in the following equation with potassium hydrogen phthalate (KHP), which serves as a reference substance:

$$2\ KC_8H_5O_4 + 10\ K_2Cr_2O_7 + 41\ H_2SO_4 \rightarrow 16\ CO_2 + 46\ H_2O + 10\ Cr_2(SO_4)_3 + 11\ K_2SO_4$$

Since each molecule of potassium dichromate $K_2Cr_2O_7$ has the same oxidizing power as 1.5 O_2 molecules, the equivalent reaction is:

$$2\ KC_8H_5O_4 + 15\ O_2 + H_2SO_4 \longrightarrow 16\ CO_2 + 6\ H_2O + K_2SO_4$$

$KC_8H_5O_4$ = potassium hydrogen phthalate

$K_2Cr_2O_7$ = potassium dichromate

H_2SO_4 = sulfuric acid

$Cr_2(SO_4)_3$ = Cr(III) sulfate

K_2SO_4 = potassium sulfate

As described above, two molecules of KHP consume 15 oxygen molecules. Therefore, the theoretical COD for one milligram KHP is 1.175 milligrams of oxygen O_2.

Advantages of the *NANOCOLOR*® analysis system compared to DIN 38 409 H41

- Reduced amounts of toxic mercury
- Generally lower quantities of toxic and hazardous reagents
- All reagents are pre-filled in the test tubes
- Significantly reduced risk of accidents for the user
- Reproducible results thanks to photometric evaluation

4.1.3.2 Sample preservation

- The sample should be thoroughly mixed or homogenized in a blender to be as representative as possible for the COD of the water to be examined.
- COD determinations should be performed as soon as possible after sampling. If this is not possible, the pH should be reduced to 2 or less by the addition of 2 mL of concentrated sulfuric acid H_2SO_4 per 1 L of sample.

- Storage of the acidified sample at room temperature: Analysis within 7 days.
- Storage of the acidified sample at 4 °C: Analysis within 28 days.

4.1.3.3 Tips & tricks

Decomposition

- Rapid decomposition is not possible for all COD tests. Depending on the composition of the test, the water content can be higher. This results in a higher vapor pressure during the decomposition and increases the risk for bursting of the test tube. For more information about decomposition, please see the respective instruction leaflet.

Rapid decomposition is not possible for all COD tests.

Background information

- PHP (potassium hydrogen phthalate) is used as a reference substance.
- *NANOCOLOR*® COD tube tests have advantages over the German norm DIN 38409-H41 in terms of use of toxic chemical compounds and user-friendly handling. Furthermore, seven *NANOCOLOR*® COD tests meet the requirements of the DIN ISO 15705:2002 standard.

Filtration

- For cumulative parameters, the sample must not be filtered prior to decomposition! By filtration, compounds which are poorly soluble are removed. Those compounds would thereby escape the detection which would lead to wrong results.
- For a determination of dissolved COD, filtration of turbid samples using the membrane filtration kit 0.45 µm (REF 916 50 / 916 52) or glass fiber paper MN 85/90 BF is recommended. These filters are tested and validated specifically for this purpose.

For cumulative parameters, the sample must not be filtered prior to decomposition.

Sea water suitability

- Sea water analysis is generally not possible because of chloride interferences.

Interferences

· At high chloride concentrations, the sample must be either diluted or the chloride-masking agent must be used. Low chloride concentrations are masked by the mercury(II) sulfate present in the test tube. The amount of chloride, which can be masked, is indicated in the respective instruction leaflets.

Turbidity

· For COD tube tests with a negative measurement direction (up to and including COD 300), turbidity leads to lower apparent results.

· For COD round cuvettes with positive measurement direction (from and including COD 600), turbidity leads to higher apparent results.

Dilution

· Special COD-free water should be always used for dilutions.

4.1.4 Nitrate (NO_3^-)

Nitrate ions are present at varying concentrations (usually up to ≈ 20 mg/L) in ground and surface waters, as well as in municipal and industrial wastewaters. They are present almost exclusively in dissolved form in water samples. Nitrate levels of 15–50 mg/L indicate anthropogenic influences. They enter municipal wastewaters e.g. as the end product of nitrification (see also 4.1.5: Nitrification, page 43, or 4.1.1: Ammonium (NH_4^+), page 35).

Nitrification is the bacterial oxidation of ammonia and other nitrogen-containing organic compounds. These emerge in large quantities as human and animal excretions or from decay processes of organic substances. Nitrates in surface and groundwaters can also originate from water-soluble components of artificial fertilizers.

Nitrate and the other nitrogen parameters ammonium and nitrite, are thus a measure for the contamination of a water body. It is important whether an increased nitrate content is linked to similarly increased ammonia and nitrite concentrations to evaluate the self-purification capacity of a water body.

Nitrate is a pollution indicator and one of the most important chemical parameters for the control of drinking water quality.

If this is not the case, the self-purification capacity is sufficient for the mineralization of organic matter. The nitrate concentration is one of the most important chemical parameters to check the quality of drinking water. The EC guide value is 25 mg/L.

Detailed information about the nitrite and ammonium concentration as well as their relationships is essential for a proper assessment of drinking water. So-called reducing conditions are present if high ammonium and low nitrate levels are observed e.g. in a (ground)water polluted with nitrogen compounds. This nitrate reduction is effected among others by bacteria and fungi (Streptomyces). Under oxygen-deficient conditions (O_2 < 5 mg/L), nitrate (NO_3^-) is first reduced to nitrite (NO_2^-), which is then degraded further e.g. to elemental nitrogen gas (N_2). Other bacteria, by contrast, reduce nitrite (NO_2^-) to ammonium (NH_4^+). The conditions are opposite in native, oxygen-rich groundwater. Here oxidation of ammonium (NH_4^+) and nitrite (NO_2^-) to nitrate (NO_3^-) by nitrogen bacteria (Nitrosomonas, Nitrococcus, Nitrobacter) takes place.

There is always pollution, if high nitrate concentrations cannot be attributed geologically to natural saltpeter deposits (especially in case of presence in groundwater).

Nitrate and nitrite are widely used as additives in the preparation of meat products ("curing"). On the one hand, the shelf life is extended by inhibition of putrefying bacteria. On the other hand, the heat- and storage-stable red curing color is formed (generation of the typical cured flavor), by the addition of nitric oxide (NO) to the muscle pigment myoglobin to form nitrogen oxide myoglobin.

The pollution of groundwater by nitrate is a serious deterioration of the environmental quality. Elevated nitrate levels have a negative impact on the ecology of the waters. They can also lead to a lower drinking water quality and thus to negative health effects. In the organism, nitrate can be converted, among other things, to nitrite, which inhibits oxygen transport by the red blood pigment (hemoglobin).

Nitrate is primarily almost non-toxic (gastric inflammation usually occurs only at levels > 500 mg/L NO_3^-). The dangers from nitrates arise from the fact that they are partially converted to nitrites by bacteria in the body (see 4.1.6: Nitrite (NO_2^-), page 46). Tertiary conversion products of nitrate (in the human body, from amines and nitrite) can be *N*-nitroso compounds, which are classified as carcinogenic. Nitrate, depending on the dose, inhibits the iodide transport mechanisms of the human organism.

With regard to human nutrition, especially some strongly nitrate-containing vegetables such as spinach, soy beans, chard, beets or radishes are to be named.

The notation of nitrate is NO_3^-, but often NO_3-N is used instead. The difference is that in NO_3-N only the mass of nitrogen is taken for account. The mass of oxygen in the nitrate is disregarded. The conversion factor is 4.43, which results from the large mass difference of nitrogen and nitrate (see section 5.1.6: Unit, page 84).

mg/L NO_3^-	mg/L NO_3-N
1	0.2
5	1.1
10	2.3
20	4.5
50	11
90	20

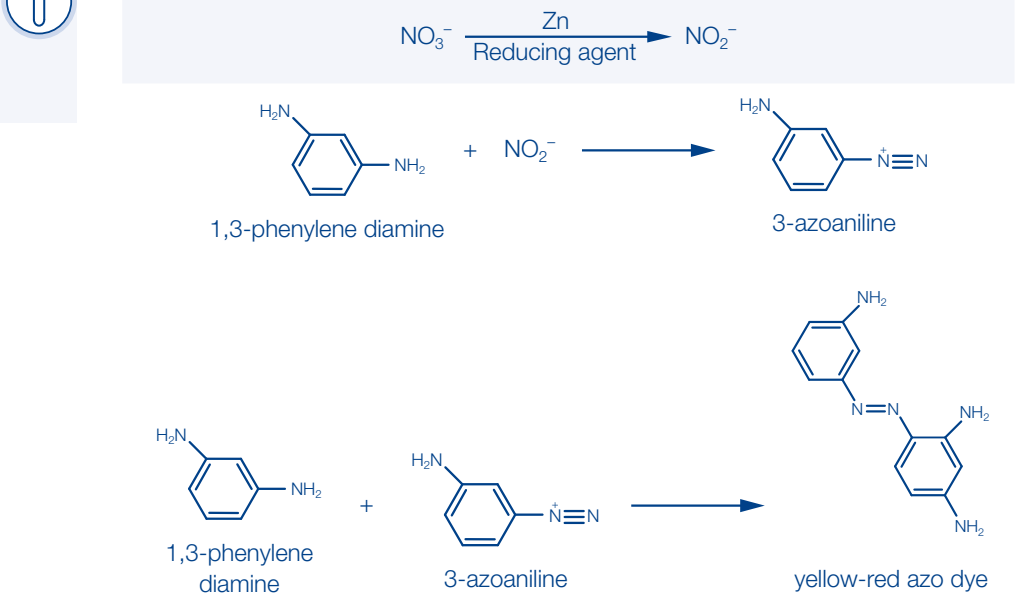
Table 5: Conversion table mg/L NO_3^-, mg/L NO_3-N

4.1.4.1 Reaction basis

Depending on the product range (*VISOCOLOR*® or *NANOCOLOR*®) and test kit, one of two different reactions is underlying:

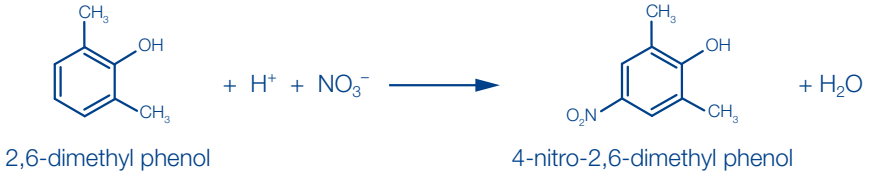
(a) **Reduction method:** In many detection methods, nitrate is reduced to nitrite in the first step. The second step is then a diazotization of an aromatic amine with the nitrite formed. This is followed by a coupling reaction to form a yellowish-red azo dye (*VISOCOLOR*®). In the standard test, the reaction is carried out with sulfanilic acid and 1-naphthylamine after the reduction to nitrite to form a red azo dye.

NO_3^- = nitrate ion
Zn = zinc
NO_2^- = nitrite ion



(b) **ISO and DIN method:** A second detection method is the photometric determination as 4-nitro-2,6-dimethylphenol, in analogy to the norms ISO 7890-1 and DIN 38405-D9-2.

The reaction uses 2,6-dimethylphenol in a mixture of sulfuric acid and phosphoric acid. Direct nitration of dimethylphenol results in the formation of 4-nitro-2,6-dimethylphenol, depending on the nitrate content of the sample.



4.1.4.2 Sample preservation

· By adjusting the pH to 1-2 with sulfuric acid, the sample can be stored for up to 7 days (storage vessel: PE bottle). Ideally, storage and transport are carried out at 4 °C in the dark.

4.1.4.3 Tips & tricks

Common sources of error

· Insufficient dissolution of the reagents causes the risk of findings below the actual value.

Background information

· The filling level of the cuvette in standard tests must be at least half of the maximum due to the beam path of the spectrophotometers.

Sea water suitability

· The *VISOCOLOR*® nitrate tests are suitable for seawater analysis. For detailed information, please refer to the respective instruction leaflet. *NANOCOLOR*® nitrate tests are only partially suitable for seawater analysis, which is due to chloride interferences. Chloride can be removed either by dilution or by use of cartridges for chloride elimination (REF 963 911).

pH

· The pH values of the sample solution stated in the package inserts must be complied with. If necessary, adjust the pH with sulfuric acid or sodium hydroxide.

Reaction temperature

· The temperature of the sample should be in the range of 18–30 °C. Especially at lower temperatures, the reaction proceeds much more slowly and may therefore lead to lower apparent results.

Interferences

· Oxidizing substances may lead to lower apparent results or even completely inhibit the reaction depending on their concentration.

· Chlorine > 10 mg/L interferes.

· Nitrite interferes from 1 mg/L (identical underlying reaction). Nitrite must be determined in advance and removed before the measurement. Nitrite is eliminated by the addition of sulfamic acid (REF 918 973) [1 measuring spoon to 10 mL of sample solution, wait with the determination of nitrate for 10 min. The pH of the solution should be in the range of 2–3, otherwise adjust with sulfuric acid].

· Organic colloids, humic acids, colored heavy metal ions as well as oxidizing and reducing substances interfere.

· Nitrate analysis is generally disturbed by peroxides which can cause a rust-brown color.

· The standard test Nitrat Z has a very sensitive measuring range and is based on the reduction method. The test cannot be applied if any other reducible substances are present.

· Further interfering ions are listed in the instruction leaflets.

Turbidity

· Turbid samples have to be filtered; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

4.1.5 Nitrification

Nitrification is performed by nitrifying bacteria.

Nitrogen is released from nitrogen-containing organic substances in the course of aerobic and anaerobic degradation processes, initially in the form of ammonium. The oxidative microbial two-stage conversion of ammonium to nitrate via nitrite is called nitrification. This process occurs in soil and water and is caused by nitrifying bacteria. This fact is exploited in wastewater treatment in sewage treatment plants.

Nitrification is an important sub-process of wastewater treatment. It is necessary to keep the concentration of ammonium ions in the effluent of sewage treatment plants as low as possible. Increased entries of ammonium into the receiving water of a sewage treatment plant can place a considerable burden on the oxygen balance of the water due to the nitrification process which starts here.

In addition, nitrite and ammonia, whose rate of release from ammonium depends on the pH and the temperature of the water, are toxic to fish, fry and other aquatic organisms. Ammonium is a major problem for many waters, also with regard to eutrophication. Not least, nitrification is also the necessary preliminary stage for denitrification in the context of complete nitrogen elimination.

Nitrificants or nitrifying bacteria are gram-negative, aerobic bacteria. A distinction is made between the groups of ammonia-oxidizing and the group of nitrite-oxidizing bacteria.

In the first sub-step of the nitrification process, ammonia-oxidizing bacteria oxidize ammonium in the presence of oxygen to nitrite.

$$2\ NH_3 + 3\ O_2 \longrightarrow 2\ NO_2^- + 2\ H^+ + 2\ H_2O$$

NH_3 = ammonia
O_2 = oxygen
NO_2^- = nitrite ion
NO_3^- = nitrate ion
H_2O = water

Subsequently, nitrite-oxidizing bacteria convert the nitrite to nitrate in the presence of oxygen in the second step.

$$2\ NO_2^- + O_2 \longrightarrow 2\ NO_3^-$$

A low nitrite content indicates a properly proceeding nitrification.

Nitrifying bacteria are very sensitive to certain environmental influences. Damages to the nitrifying element of the species community have particularly severe consequences, since they also have a much lower growth rate and a lower diversity of species than heterotrophic bacteria.

A number of substances are known for a long time inhibiting nitrification selectively without affecting the metabolic activity of heterotrophic bacteria significantly. Nitrifying bacteria show pronounced sensitivity to compounds such as *N*-allylthiourea (used e.g. in BOD_5 determination for inhibition of nitrification), thiourea or 2-chloro-6-trimethylpyridine (*N*-Serve), which inhibit nitrification even at very low concentrations (micromolar range). Nitrification-inhibiting substances from different sources enter treatment plants with the wastewater. Therefore, they contribute to significant, sometimes irreversible damage to the extremely sensitive nitrifying bacteria in the activated sludge. Those bacteria represent only a small proportion of the dry matter of the sludge. These inhibitors can cause major problems to the affected facilities, which results in enormous additional costs.

Since 1995, there has been the norm DIN EN ISO 9509-L38 to determine the inhibitory effect of water samples and chemicals on nitrification.

The importance of this problem is also reflected by the fact that in Germany exists a DIN standard for the determination of the nitrification inhibitory effect of water samples and chemicals exists since April 1995 (DIN EN ISO 9509-L38 2006-10: “Method for determining the nitrification inhibition of micro-organisms in activated sludge by substances and wastewater.”).

According to this DIN, nitrifying activated sludge of undefined microbial composition from sewage treatment plants with predominantly municipal wastewater is used as biomass. The test duration is four hours. The concentrations of the nitrogen parameters ammonium-N, nitrite-N and nitrate-N in mg/L in the sample preparation compared to a parallel control preparation without inhibition are the parameters and assessment principles. Aeration and agitation of the test mixtures during incubation is indispensable.

A significant disadvantage of the DIN method is the insufficient reproducibility and standardization of the results due to the use of a sludge biomass which is completely undefined in terms of qualitative and quantitative species composition of nitrifying bacteria. The high effort in terms of time and labor for the preparation and provision of the activated sludge sample, which is used as biomass, as well as the actual incubation of the test samples of 4 hours, have a very negative effect. The final determination of concentrations of the nitrogen parameters ammonium-N, nitrite-N and nitrate-N in the individual test samples e.g. by photometric methods is likewise laborious and time-consuming. Therefore an overall expenditure of at least one working day must be considered for the performance of a DIN test.

In addition to the nitrification, there is also the opposite process, the denitrification. During denitrification, C-heterotrophic bacteria (denitrifying bacteria) reduce nitrate, via nitrite as an intermediate, to elemental nitrogen gas, N_2. This requires a low-oxygen environment.

4.1.5.1 Reaction basis

The nitrification inhibition tests BioFix® *A-Tox* and BioFix® *N-Tox* are based on an amperometric measurement of oxygen consumption.

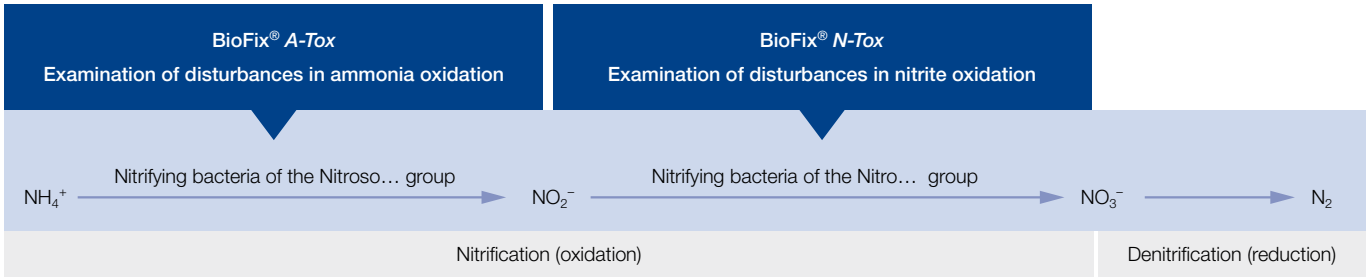


Figure 23: Use of the BioFix® nitrification inhibition tests

Nitrifying microbial strains which are typical for sewage treatment plants, preferable of the genera Nitrosomonas and Nitrobacter, are used as biomass. Here the bacterial strains are used with defined composition, both, to the precise bacterial strain as well as to their concentration. They are used as inoculates in the assay mixture separately as pure cultures or alternatively as mixed cultures. The metabolic activity of the test organisms is measured using a commercially available oxygen electrode. The result is given as % inhibition of the oxygen consumption of the sample solution in comparison to an uninhibited control.

The Biofix® nitrification inhibition tests permit the following examinations:

1) Targeted examination using the BioFix® *A-Tox* test to check whether the first stage of nitrification, ammonia oxidation, is inhibited by substances in the sample.
2) Targeted examination using the BioFix® *N-Tox* test to check whether the second stage of nitrification, nitrite oxidation, is inhibited by substances in the sample.
3) Undifferentiated screening testing A-/*N-Tox* using both BioFix® tests (*A-Tox* and *N-Tox*) to examine whether nitrification in general is inhibited by substances in the sample.

Significant advantages of the Biofix® nitrification inhibition tests over the DIN test

- Higher sensitivity
- Speed and time savings (test duration of 10 min <--> DIN test: four hours)
- Significantly less labor effort and easy performance (results after 30–60 min <--> DIN test: 1–1½ days)
- Very good reproducibility of the results, since defined bacterial strains in defined concentrations are used
- Ready-to-use reagents
- Possibility of differentiated examination as to which stage of nitrification is inhibited (ammonia and /or nitrite oxidation)
- Preserved nitrifying bacteria for use in accordance with the norm DIN EN ISO 9509-L38

4.1.5.2 Tips & tricks

Performance of the test

- Uniform stirring (always ensure identical stirring speed) is crucial for accurate and reproducible results. Shaking is not sufficient and in particular not uniform enough to enrich the sample sufficiently with O_2.
- The baseline oxygen level in control and sample must be nearly identical; the deviation may not exceed 0.1–0.4 mg/L O_2.
- A stable oxygen value before the addition of reagent R3 is crucial; optionally wait at this point until a stable value has been reached.
- The oxygen concentration in the control may decrease to a minimum of 1 mg/L O_2. No reasonable calculation is possible in the evaluation in case of a stronger decrease. Hence, plausible results cannot be obtained. In this case it may be necessary to end the measurement sooner (than the 10 min specified). However, it is important that the same reaction time is also used in the oxygen measurement of the sample.

Compatible oxygen probes

In principle, any oxygen electrode that fits into the adapter from the starter kit can be used. The adapter has an inner diameter of 16 mm. Thus, the electrode needs to have an outer diameter of 15–16 mm.

Alternatively, thinner probes with an outer diameter of 12 mm can be used. In this case additionally a special adapter (REF 970 116) is required. If you have further questions about the test performance and about compatible oxygen probes, please contact MACHEREY-NAGEL directly, or ask your local sales representative.

4.1.6 Nitrite (NO_2^-)

Nitrite ions are present in low concentrations in surface waters and rarely in groundwaters. In wastewaters, by contrast, nitrite concentrations are often higher. Nitrite ions are present in water almost exclusively in dissolved form. Higher nitrite concentrations in wastewaters suggest either industrial effluents (metal pickling agents, chemical industry) or fecal contamination (decomposition product of nitrification: nitrite is produced during the bacterial oxidation of ammonia and in the reduction of nitrate) (see also 4.1.5: Nitrification, page 43).

Another source of nitrite formation from nitrate are of galvanized iron pipes of domestic installations. Concentrations up to 1 mg/L are still classified as harmless. A major field of application of nitrites is the manufacture of dyes.

Nitrites are toxic since they block the blood pigment hemoglobin and thus the transport of oxygen.

In adults, reduction of nitrate to nitrite takes place in the small intestine, whereas in infants this occurs already in the stomach. Nitrites are toxic to humans. They block the blood pigment hemoglobin, which is necessary for oxygen transport. Especially in infants, life-threatening conditions with acute suffocation may occur (infant cyanosis = methemoglobinaemia). In addition, nitrites are also involved in the formation of carcinogenic nitrosamines.

Nitrites have high and pH-dependent toxicity to fish.

According to the German Drinking Water Ordinance (TrinkwV), limits are 0.1 mg/L in the outflow of sewage treatment plants, and 0.5 mg/L in the tap.

Despite their toxicity, nitrites have numerous applications. They are used e.g. as food additives or in the production of sausages as nitrite curing salt. In general, an increase in nitrite content is always a sign of bacterial contamination. These can be detected early by a nitrite measurement, which is also an important parameter in cooling lubricants. Nitrites react with cooling lubricants to form carcinogenic nitrosamines, which can enter the human body as aerosols.

NO_2-N is frequently used as notation rather than NO_2^-, which indicates that only the mass of nitrogen of the nitrite ion is taken for account while the oxygen atoms are neglected. The conversion factor of NO_2-N to NO_2^- is 3.28, resulting from the atomic masses (see section 5.1.6: Unit, page 84).

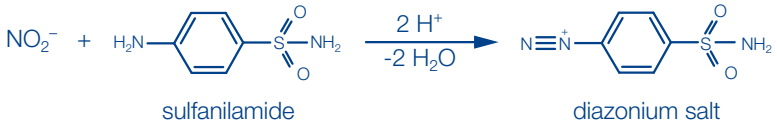
mg/L NO_2^-	mg/L NO_2-N
0.02	0.006
0.05	0.015
0.1	0.03
0.2	0.06
0.5	0.15

Table 6: Conversion table mg/L NO_2^-, mg/L NO_2-N

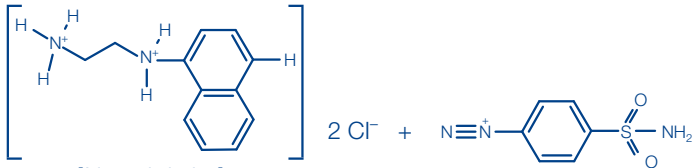
4.1.6.1 Reaction basis

Depending on the product range (*VISOCOLOR*® or *NANOCOLOR*®) and test kit, one of two different reactions is underlying:

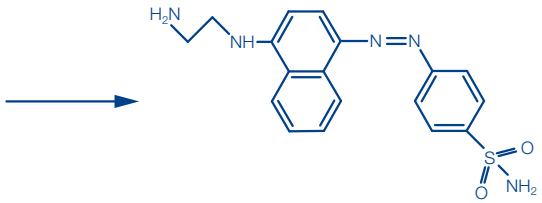
(a) **ISO method in analogy to ISO 6777:** Nitrite reacts with sulfanilamide and *N*-(1-naphthyl)-ethylenediamine to form a purple azo dye. The underlying reaction is also analogous to DIN EN 26777-D10, APHA 4500-NH_2 and EPA 354.1.



sulfanilamide — diazonium salt



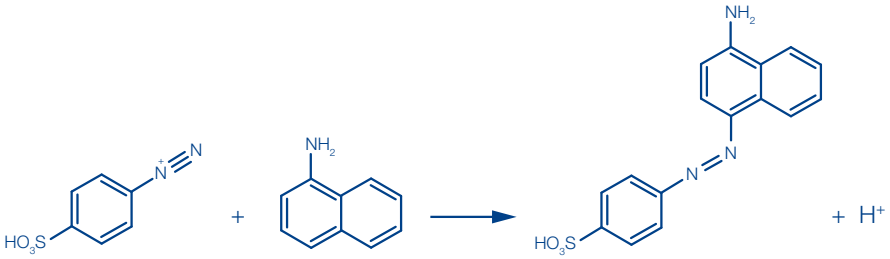
[*N*-naphthyl-1]-ethylenediamine — diazonium salt



azo dye

(b) **Sulfanilic acid method (Griess-Ilosvay reaction):** Sulfanilic acid is diazotized by nitrite in acidic solution. The diazonium salt which is formed is then coupled with 1-naphthylamine to form a red azo dye.

sulfanilic acid — diazonium ion



diazonium ion — 1-naphthyl amine — azo dye (red)

4.1.6.2 Sample preservation

· The sample can be stored max. 1 day (storage vessel: PE bottle) and should be measured quickly. Ideally, storage and transport are carried out at 4 °C in the dark.

4.1.6.3 Tips & tricks

Background information

· The reagents for sample preparation by clarification precipitation (REF 918 937) can be used for removal of emulsions, turbidity and color prior to the nitrite determination, e.g. in cooling lubricants, landfill leachate, etc.,.

· Additionally a blank value should be measured for nitrite measurements in heavily contaminated samples (e.g. in inlet waters).

Sea water suitability

· All *VISOCOLOR*® and *NANOCOLOR*® nitrite tests are suitable for seawater analysis.

pH

· The pH values for the sample solution stated in the instruction leaflet must be complied with. If necessary, adjust the pH with hydrochloric acid or sodium hydroxide.

Interferences

· Organic colloids, chlorine, humic acids and colored heavy metal ions interfere.

· Further interfering ions are listed in the instruction leaflets.

Turbidity

· Turbid samples have to be filtered; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

4.1.7 Phosphate (PO_4^{3-})

Inorganic and organic phosphorus compounds are now found in almost all municipal and industrial wastewaters. They are predominantly present in the form of ortho-, poly- or organo-phosphates. The commonality is the basic structure of phosphate, PO_4^{3-}.

In condensation reactions under heating, ortho-phosphate reacts to form its polymeric acids and salts:

$$2\ H_3PO_4 \xrightarrow{\Delta T} H_4P_2O_7 + H_2O$$

H_3PO_4 = ortho-phosphoric acid
$H_4P_2O_7$ = diphosphoric acid

Together with nitrogen and potassium compounds, phosphates are among the most important fertilizers for adequate plant growth. In addition, phosphates are added as detergent additives for water softening and as preservatives in foodstuffs, since they inhibit growth of fungi and bacteria. However, their use as a water softener is declining, since too high phosphate levels in waters lead to over-fertilization and ultimately to “collapse”.

Phosphates are important fertilizers.

Moreover, natural phosphate resources are limited. Therefore, increasingly efforts are made to recover phosphorus from sewage sludge in wastewater treatment plants. This is done primarily with biological phosphorus removal, since the availability of phosphorus in its natural form is not unlimited.

The phosphate content of surface water determines its trophic status.

The phosphate content of surface water determines its trophic status. Very high phosphate levels lead to eutrophication (over-fertilization: increased growth of algae and aquatic plants) of rivers and lakes and can ultimately lead to extinction of plants and fish. Pure waters, e.g. mountain streams, have phosphate levels of < 0.1 mg/L PO_4^{3-}, usually even less than 0.03 mg/L PO_4^{3-}. Concentrations above 0.1 mg/L PO_4^{3-} are only connected to pollution only if other pollution parameters are positive as well. Phosphate levels above 0.3 mg/L PO_4^{3-} are an indication of pollution (special cases are swamp waters with levels of up to 1 mg/L PO_4^{3-}). A high phosphate content is a reliable chemical indicator in case of fecal contaminations. Even normal levels may be determined in polluted deeper groundwaters, because some soils can absorb phosphates.

Phosphates are of importance for pipe networks with aggressive waters, due to the formation of protective coatings. However, for adequate formation 0.1 mg/L (max. 1 mg/L) are already sufficient.

A general distinction has to be made between inorganic phosphorus compounds (phosphate or hydrogen phosphate ions and polyphosphates) and organically bound phosphorus. Polyphosphates and organically bound phosphorus can be determined only after oxidative decomposition (“destruction”).

Phosphates play an important role for humans in bone formation in the form of calcium phosphate. They are also important in energy metabolism. However as little phosphate as possible should be present in drinking water, since excessive amounts can lead to digestive upset and are suspected of triggering kidney problems as well.

The main entry of phosphates is with municipal wastewaters (cleaning products) and agriculture (fertilizers). Phosphates must be removed from wastewater, since higher amounts will result in a eutrophication of the receiving water.

Phosphates can be eliminated chemically or biologically:

In chemical phosphorus precipitation, soluble phosphates are converted into insoluble compounds by the addition of suitable precipitating agents and are thus removed from the solution by precipitation. Iron chlorides and sulfates, aluminum salts or lime are used as precipitation agents.

In biological phosphorus removal (Bio-P), micro-organisms are used. They are deprived of oxygen in an anaerobic basin. They release stored phosphates for energy production to survive. When the micro-organisms are then supplied with oxygen again, they absorb the previously released phosphates and other phosphates in the solution. Hence, the phosphate content in the basin is reduced.

Further notations are used in addition to the phosphate ion (PO_4^{3-}) in many tests. The notation PO_4–P is often used which reflects only the phosphorus content and disregards the oxygen content, comparable to the nitrogen parameters ammonium, nitrate and nitrite. The conversion factor of PO_4–P to PO_4^{3-} is 3.07.

mg/L PO_4^{3-}	mg/L P_2O_5	mg/L PO_4–P
0.6	0.5	0.2
1.5	1.1	0.5
3	2	1
6	5	2
15	12	5

Table 7: Conversion table mg/L PO_4^{3-}, mg/L P_2O_5 and mg/L PO_4–P

Phosphates can be eliminated chemically or biologically.

4.1.7.1 Reaction basis

Depending on the product range (*VISOCOLOR*® or *NANOCOLOR*®) and test kit, one of two different reactions is underlying:

(a) **DIN method in analogy to DIN EN ISO 6878-D11, APHA 4500-PE as well as EPA 365.2 and 365.3.:** Ammonium molybdate reacts with ortho-phosphate ions to form phosphomolybdic acid. This is reduced with a reducing agent to phosphorus molybdenum blue. Acidic oxidation at 100–120 °C is performed for the determination of total phosphate, to include poly- and organophosphates.

$$PO_4^{3-} + 12\ MoO_4^{2-} + 24\ H^+ + 3\ NH_4^+ \longrightarrow (NH_4)_3[P(Mo_3O_{10})_4] + 12\ H_2O \xrightarrow[\text{reduction}]{Na_2S_2O_5} \text{phosphorus molybdenum blue}$$

(b) **Vanadate method:** ortho-phosphate ions react with molybdate and vanadate ions to form a yellow phosphoric acid/molybdate/vanadate complex. The underlying reaction is also analogous to APHA 4500-P C.

$$PO_4^{3-} + 2\ VO_3^- + 10\ MoO_4^{2-} + 10\ H_2O \longrightarrow [PV_2Mo_{10}O_{40}]^{5-} + 20\ OH^-$$

PO_4^{3-} = phosphate ion
MoO_4^{2-} = molybdenum(VI) oxide
NH_4^+ = ammonium ion
$(NH_4)_3[P(Mo_3O_{10})_4]$ = phosphomolybdic acid
$Na_2S_2O_5$ = sodium disulfite
$Mo_4O_{10}(OH)_2$ = molybdenum blue
VO_3^- = vanadate ion
$[PV_2Mo_{10}O_{40}]^{5-}$ = phosphoric acid / molybdate / vanadate complex

4.1.7.2 Sample preservation

- The sample can be stored for up to 7 days by adjusting the pH to 1-2 with sulfuric acid. (Storage vessel: PE bottle). Ideally, storage and transport are carried out at 4 °C in the dark.
- Generally, cooling of the sample is recommended.
- The phosphate portion, which is not present as ortho-phosphate, occurs in sewage treatment plants mostly in the form of sludge particles. The total phosphate content is thus affected by the content of suspended matter. Accordingly, a sample representative with respect to the suspended matter must be taken. In addition, a careful homogenization of the sample (by Ultra-Turrax® or magnetic stirrer) must be performed prior to determination. Any cooled samples should be brought to room temperature before homogenization. Homogenized samples must be analyzed immediately!
- If only the ortho-phosphate content of a sample containing suspended matter is to be determined, it must be filtered as quickly as possible.

4.1.7.3 Tips & tricks

Decomposition

· Decomposition with *NANOCOLOR*® *NanOx* Metal (REF 918 978) is recommended in case of an elevated content of organic materials and/or organically bound phosphorus.

· An incomplete decomposition leads to lower apparent results and possibly to lower total phosphate than ortho-phosphate levels.

For cumulative parameters, the sample must not be filtered prior to decomposition.

Filtration

· For cumulative parameters, the sample must not be filtered prior to decomposition! Compounds which are poorly soluble are removed by filtration. Those compounds would thereby escape a detection which would lead to wrong results.

· In the determination of ortho-phosphate, on the other hand, filtration is performed prior to analysis. Turbid samples have to be filtered; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

· Any precipitates which are present after the decomposition can be removed using membrane filters before determination.

Common sources of errors

· Carryover of phosphoric acid (e.g. from the tube test *NANOCOLOR*® Nitrate 50): Nitrate is measured frequently before the determination of phosphate. The nitrate test comprises phosphoric acid. The failure not to change the pipette tip may result in carryover and thus in higher apparent phosphate. A carryover takes place even if only the top edge of the nitrate test tube has touched the pipette tip.

Ortho-phosphates are directly amenable to analysis. For the determination of total phosphate, previous decomposition is required.

Background information

· Difference between ortho- and total phosphate:

- Ortho-phosphates are readily soluble, usually inorganic salts of phosphoric acid. These compounds are directly accessible to analysis and do not require a decomposition.
- In addition to the readily soluble ortho-phosphates also poly- and organo-phosphates are determined in total phosphate determination. The latter are not directly accessible to the analysis reaction. The poly- and organo-phosphates are converted into ortho-phosphates by an acidic decomposition at 100–120 °C and can thus be detected as well. These hard-to-oxidize phosphate compounds can be decomposed with *NANOCOLOR*® *NanOx* Metal (REF 918 978).

· Generally, for determination of phosphate with our products, the phosphates must be present as ortho-phosphates.

Homogenization

· The use of an inhomogeneous sample for a determination of total phosphate can lead to underestimated results.

Sea water suitability

· All *VISOCOLOR*® and *NANOCOLOR*® phosphate tests are suitable for seawater analysis.

pH

· The pH values of the sample solution that are stated in the package inserts must be complied with. If necessary, adjust the pH with sulfuric acid.

Interferences

· Any interference by silica can be eliminated by the addition of citric acid.

· Further interfering ions are listed in the instruction leaflet.

Turbidity

· Turbid samples have to be filtered; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

· Turbidity can lead to apparently lower total phosphate than ortho-phosphate content.

4.1.8 Total nitrogen (TN_b)

Total nitrogen (TN_b) is a cumulative parameter. TN_b stands for total bound nitrogen.

Both organic nitrogen (urea, peptides, proteins) and inorganic or mineral nitrogen (ammonium/ammonia, nitrate, nitrite, see the respective parameters) are detected. Gaseous elemental nitrogen N_2 which is contained in the water cannot be determined.

As the first inorganic degradation product during bacterial nitrification ammonium NH_4^+ is obtained, which then reacts via the labile intermediate nitrite NO_2^- to ultimately form nitrate NO_3^- (see also 4.1.5: Nitrification, page 43).

One goal of water protection is to protect surface waters against eutrophication from excessive entry of e.g. nitrogen compounds (excessive nutrient loads). To achieve this, the water protection provided by federal and state governments provides for certain discharge conditions which are defined in the water discharge permits, and self-control regulations in the respective states. Important processes for degradation of nitrogen compounds include nitrification and denitrification. Control and optimization of such processes is based on the use and proper documentation of appropriate methods of analysis.

The term Total Kjeldahl Nitrogen (TKN) is defined as the total amount of organically bound nitrogen and ammonia nitrogen. In the presence of detectable amounts of nitrate/nitrite, TKN can be calculated by subtracting the nitrate/nitrite nitrogen from total nitrogen TN_b.

Kjeldahl nitrogen is the sum of organically bound and ammonium nitrogen.

The relationship between these parameters in nitrogen analysis is summarized in the following flow chart:

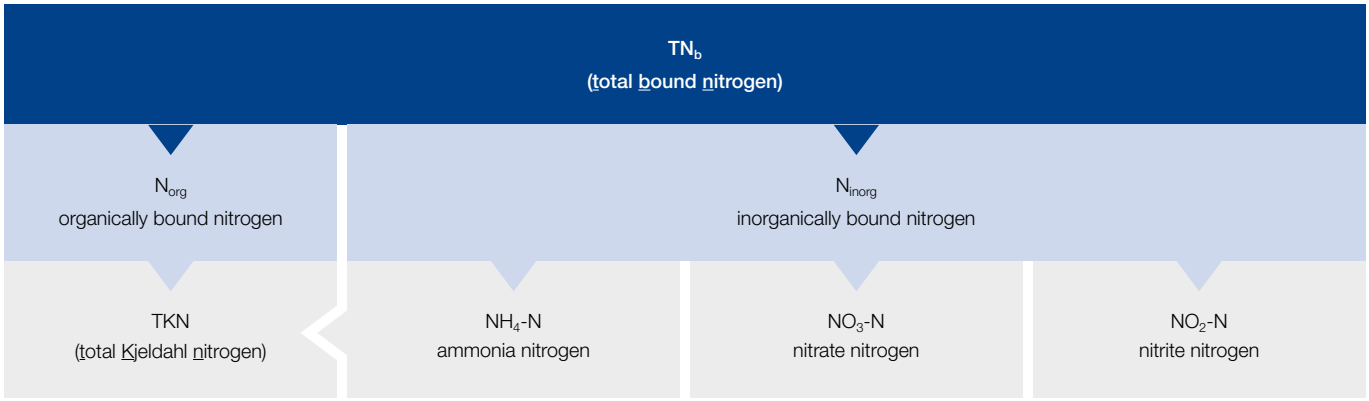


Figure 24: Relationships between nitrogen compound parameters

In summary, this means that the nitrogen compounds present in water bodies are mainly degradation or decomposition products of substances containing organic nitrogen (primarily proteins and urea).

4.1.8.1 Reaction basis

In an acidic medium, all organic and inorganic nitrogen-containing substances are oxidized to nitrate (in analogy to ISO 7890-1).

The underlying reaction is also analogous to DIN EN ISO 11905-1 and DIN 38405-D9.

Nitrate reacts in acidic solution with 2,6-dimethylphenol to form 4-nitro-2,6-dimethylphenol, which can be determined photometrically. In samples with low nitrate and nitrite concentrations, this method (in analogy to ISO 7890-1) yields results similar to the determination of TKN (covering only ammonium and organic nitrogen compounds). In case of detectable amounts of nitrate and nitrite, the TKN value can be determined by subtracting the nitrate/nitrite values from the total nitrogen value TN_b.

4.1.8.2 Sample preservation

- After stabilization of the pH with H_2SO_4 to pH 1–2, the sample can be stored for 7 days until the start of analysis (storage vessel: PE or glass bottle).
- The sample taken should be as representative as possible of the TN_b of the water to be examined and thus thoroughly mixed or homogenized in a blender.

4.1.8.3 Tips & tricks

For cumulative parameters, the sample is not to be filtered prior to decomposition.

Filtration

- For cumulative parameters, the sample must not be filtered prior to decomposition! By filtration, poorly soluble nitrogen compounds are removed and can thus not be detected. Thereby incorrect results are obtained.

pH

- The pH of the sample to be decomposed must be between 5 and 9. If necessary, adjust the pH with sulfuric acid or sodium hydroxide.

Interferences

- Nitrogen concentrations above the double measuring range can simulate measured values that lie within the simple measuring range and may thus be misinterpreted.
- There is a risk of incomplete decomposition for samples that consume large amounts of oxidizing agents (e.g. having COD values above 5000 mg/L O_2). In these cases, the decomposition has to be repeated with the original sample diluted before.

Sea water suitability

- The *NANOCOLOR*® total Nitrogen TN_b tests are not suitable for seawater analysis.

4.1.9 TOC

Total organic carbon (TOC) is, in addition to COD and BOD_5, an important cumulative parameter for assessing the organic contamination of water. It comprises the three different parameters DOC, POC and VOC:

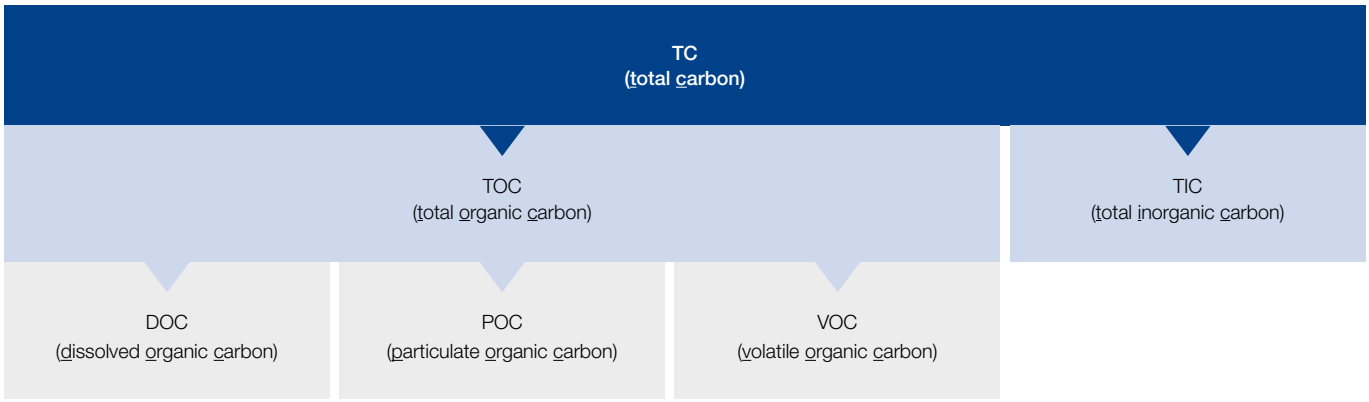


Figure 25: Relationship between carbon compounds

The TOC value comprises the total carbon of organic compounds dissolved in water, as well as insoluble carbon which is not belonging to carbonic acid or its salts. Together with the TIC (total inorganic carbon) value, the TOC covers all the carbon.

The TOC is a measure for the contamination of water with organic substances. These may be hazardous for water even in trace amounts. It should be noted that this value does not say anything about the nature of the compounds present in water and thus is no direct indicator of potential health risks. In contrast to the COD, here even poorly degradable substances are determined.

Waters with low contamination have a TOC of about 1–2 mg/L C. In strongly polluted waters (increase e.g. by algal blooms), values of up to 10 mg/L C can be achieved.

The TOC content in potable water is usually between 0.5 and 2 mg/L C. Elevated concentrations of organic matter in the water are undesirable, because they are on the one hand used by micro-organisms as a growth medium for propagation, and on the other are partially precursors of toxic trihalomethanes (THMs).

4.1.9.1 Reaction basis

The organic carbon in the sample is oxidized to carbon dioxide (CO_2) for the determination. The CO_2 gas diffuses through a membrane into an indicator solution. The occurring color change of the solution is then evaluated photometrically. The inorganic carbon content is removed from the sample prior to oxidation by acidification and subsequent expulsion as CO_2 ("purging") to prevent interference.

In summary, TOC detection can be broken down into the following three analysis steps:

1) Removal of inorganic carbon (TIC = total inorganic carbon) with an acid

$$CO_3^{2-} + 2\,H^+ \longrightarrow CO_2\uparrow + H_2O$$

or

$$HCO_3^- + H^+ \longrightarrow CO_2\uparrow + H_2O$$

2) Oxidation of all (organic) carbon compounds in the sample to carbon dioxide CO_2

3) Quantitative detection of the CO_2 formed by with an indicator (underlying reaction in analogy to DIN EN 1484)

CO_3^{2-} = carbonate ion
H^+ = hydrogen ion
CO_2 = carbon dioxide
H_2O = water
HCO_3^- = hydrogen carbonate ion

4.1.9.2 Sample preservation

· The sample taken should be as representative as possible for the TOC of the water to be examined and thus thoroughly mixed or homogenized in a blender.

· TOC analysis should be carried out as soon as possible after sampling. If this is not possible, add 2 mL of concentrated sulfuric acid H_2SO_4 per 1 L of sample to reduce the pH should to a value of 2 or less:

- Storage of the acidified sample at room temperature: Analysis within 7 days.

- Storage of the acidified sample at 4 °C: Analysis within 28 days.

4.1.9.3 Tips & tricks

Filtration

· For cumulative parameters such as TOC, the sample must not be filtered prior to decomposition! By filtration, poorly soluble organic carbon compounds are removed and thus can not be detected. This leads to incorrect results.

· For determination of DOC (dissolved organic carbon), filtration of turbid samples using the membrane filtration kit 0.45 µm (REF 916 50 / 916 52) or the glass fiber paper MN 85/90 BF is recommended. These filters are tested and validated specifically for this purpose.

For cumulative parameters, the sample must not be filtered prior to decomposition.

Sea water suitability

· Sea water analysis is generally not possible because of a chloride interference.

pH

· The pH of the sample solution of 1–12, which is stated in the instruction leaflet, must be complied with. If necessary, adjust the pH with sulfuric acid.

Interferences

· Not expelled TIC and chloride interfere with analysis. The concentration from which on interference is to be expected is specified in the respective instruction leaflet.

Performance of the test

· To determine only the TOC, TIC must be expelled prior to analysis.

· The TIC is difficult to remove from hard water. Therefore, we recommend increasing the purging time for carbonate-rich samples (high TIC content).

Parameter	BOD	TOC	COD
Oxidant	Bio-oxidation by micro-organisms	$Na_2S_2O_8$	$K_2Cr_2O_7$
Reaction time	Usually 5 days (BOD_5; the time can be reduced by higher incubation temperatures)	Minutes to hours	30–120 minutes
Use	Assessment of treatment processes and loading effects	Measurement of total carbon in organic contaminants	Swift and frequent monitoring of treatment effectiveness
Accuracy and precision	approximately ± 15 % standard deviation	approximately ± 3–6 % standard deviation	Differing; approximately ± 5–10 % standard deviation (the better the sample was homogenized, the smaller the deviation will be)
Advantages	Natural conditions are best reproduced with proper inoculation of the sample.	Determines total organic carbon, but also hard-to-degrade substances.	Corresponds to BOD for waste components of constant composition. Toxic substances have no effect on the oxidizing agent.
Disadvantages	Toxic substances kill the micro-organisms. Micro-organisms do not oxidize all materials present in the waste. Inaccuracy caused by poor inoculation material. Long waiting time.	Only the total carbon but not the potential oxygen demand is measured.	Interferences in case of high chloride contents. Certain organic substances are oxidized only incompletely.

Table 8: General comparison of BOD, COD and TOC

4.2 Metal analysis

In the metalworking industry, the contamination level of the wastewater is caused by major chemical metal parameters. A distinction is made in the analysis between total metal, dissolved metal ions and their various oxidation states.

Useful background knowledge, information on sample preparation and preservation as well as reaction basics for the main metal parameters are explained below.

Aluminum is the most abundant metal in the earth's crust.

4.2.1 Aluminum

Aluminum is the most abundant metal in the earth's crust and the third most abundant metal among all elements. It is one of the most commonly used light metals, because of its easy deformability (ductility). In nature it is not found as a genuine metal, but in the form of oxides because of its high oxygen affinity. Aluminum compounds are present only in very low concentrations in natural waters. However, in the wastewater of aluminum pickling plants, electroplating plants and paper mills, aluminum salts are present at significantly higher levels. In sewage treatment plants, aluminum compounds are often used as precipitating agents.

Physiologically, aluminum compounds are relatively harmless to humans. However, they are phytotoxic and can thus cause plankton death with the corresponding resultant environmental detriments.

The German Drinking Water Ordinance defines a limit of 0.2 mg/L Al^{3+} (guide value according to the German Drinking Water Ordinance). The German Mineral and Table Water Ordinance likewise specifies a value of 0.2 mg/L Al^{3+}.

Aluminum compounds have many applications, for example in aluminum pickling plants, electroplating, paper mills or as flocculants for water treatment in swimming pools.

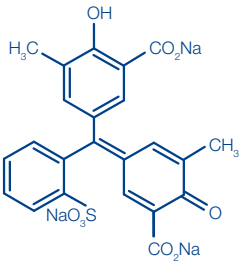
4.2.1.1 Reaction basis

Depending on the product range (*VISOCOLOR*® or *NANOCOLOR*®) and test kit, one of two different reactions is underlying:

(a) Colorimetric determination with chromazurol S (*VISOCOLOR*®)

(b) Photometric determination with eriochrome cyanine R (*NANOCOLOR*®) in analogy to APHA 3500-Al D

Al^{3+} forms a red-violet colored lacquer with eriochrome cyanine R in weakly acidic solution. Color and intensity of the lacquer material depend on the pH of the sample. Therefore, care must be taken to ensure the specified pH range of the sample solution (pH 3–6).



Eriochrome cyanine R

4.2.1.2 Sample preservation

· After adjusting the pH to 1–2 with nitric acid, the sample can be preserved for storage for up to 1 month (storage vessel: PE bottle).

4.2.1.3 Tips & tricks

Sea water suitability

· All *VISOCOLOR*® and *NANOCOLOR*® Aluminum tests are suitable for sea water analysis; some require dilution (1+9). For more information, please refer to the respective instruction leaflet.

pH

· For the tube test *NANOCOLOR*® Aluminum, highly acidic and buffered solutions have to be adjusted to pH 3–6. If necessary, adjust the pH with nitric acid or sodium hydroxide.

· The sample solution pH values stated in the package inserts must be complied with.

Interferences

· Fluoride ions interfere with all aluminum tests due to formation of very stable AlF_3 in the presence of aluminum compounds in the sample solution.

· Further interfering ions are listed in the package inserts.

Performance of the test

· The sample may not be decomposed in glass vessels for the determination of total aluminum (e.g. with the decomposition reagent *NANOCOLOR*® *NanOx* Metal), as aluminosilicates might be released from the glass, leading to higher apparent results. Alternatively, the decomposition is carried out in special vessels in a microwave oven.

For the determination of total aluminum, the sample may not be decomposed in glass vessels, as aluminosilicates might be released from the glass.

Turbidity

· Turbid solutions must be filtered prior to the determination of dissolved aluminum; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

4.2.2 Lead

In nature, lead is only rarely found as a genuine metal (pure element). In bound form, exclusively lead(II) compounds are found, especially sulfides, such as galena (PbS), and salts. Certain types of drinking water can dissolve lead compounds depending on the percentages of oxygen and free carbon dioxide. Due to use of lead pipes in water pipelines, special care should be exercised here, as lead compounds are highly toxic. This is a particular problem with soft waters. In hard water, lead carbonate and lead sulfate are formed on the inner wall of lead pipes. Thereby, the lead is protected from further attack of the water.

Lead compounds are highly toxic.

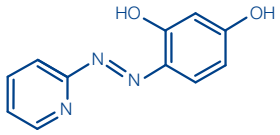
Lead is primarily used due to its very good corrosion resistance to mineral acids. In addition, it is a malleable metal with a low melting point and low hardness but high density. Therefore, lead is widely used in batteries and also for absorption of X-rays or gamma rays.

Lead compounds are toxic, since they inhibit hemoglobin synthesis.

4.2.2.1 Reaction basis

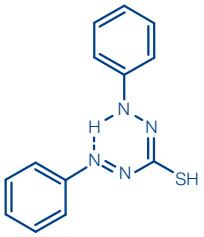
Depending on the test (*NANOCOLOR*® tube or standard test), one of two different reactions is underlying:

(a) PAR method: Lead(II) ions form a red dye with 4-(pyridyl-2-azo)resorcinol (PAR) in the presence of cyanide. In the presence of interfering heavy metals, the red dye is selectively destroyed. In this case the corresponding color weakening is evaluated photometrically. The photometric determination is carried out at 520 nm.



4-(pyridyl-2-azo)resorcinol (PAR)

(b) Dithizone method (solvent extraction method): Lead(II) ions react with dithizone (diphenyl thiocarbazone) in the presence of cyanide to form primary lead dithizonate. This is converted to a pink complex by liquid extraction in an organic phase (e.g. tetrachlorethylene or carbon tetrachloride). Dithizone ($C_{13}H_{12}N_4S$) is a powder whose needles have a purplish-black metallic sheen.



Dithizone (diphenyl thiocarbazone)

4.2.2.2 Sample preservation

· After adjusting the pH to a value of 1–2 with nitric acid, the sample can be preserved for storage for up to 1 month (storage vessel: PE or glass bottle).

4.2.2.3 Tips & tricks

Decomposition

· The decomposition cannot be performed with *NANOCOLOR*® *NanOx* Metal. The reagents therein contain carbonates that form insoluble lead carbonate with the lead ions. Detection is then no longer possible.

Background information

· Only dissolved lead(II) ions are detected. For the determination of total lead, decomposition with the decomposition kit (REF 918 08) must be performed prior to analysis.

Sea water suitability

· Sea water analysis is not possible.

pH

· The pH of the sample must be complied with in both methods.In the PAR method this is around 3–6, in the dithizone detection method at 1–3. If necessary, adjust the pH with nitric acid or sodium hydroxide.

Interferences

· Many ions influence the detection reaction with PAR, which can result in deviating results. The instruction leaflet of the tube test specifies these ions.

· Dithizone forms stable complexes with other thiophilic ("sulfur-loving") ions as well. Therefore some ions interfere. Exact specifications as to which ions interfere in what concentrations are indicated in the instruction leaflet.

· Further interfering ions are listed in the instruction leaflet.

Thiophilic = "sulfur-loving"

Turbidity

· Turbid solutions must be filtered prior to the determination of dissolved lead; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

4.2.3 Cadmium

Cadmium and its compounds are widely used in industry as corrosion protection coatings, for the production of batteries and photovoltaic cells, for bearing metals, luminescent materials and colors. In water, these compounds are present in dissolved form as cadmium(II) ions and as complex cadmium alkali cyanide. In addition, it can be present in insoluble forms such as cadmium hydroxide, carbonate or phosphate.

Cadmium compounds are also highly toxic.

Cadmium compounds are highly toxic.

4.2.3.1 Reaction basis

Depending on the test (*NANOCOLOR*® tube or standard test), one of two different reactions is underlying:

(a) **Cadion method:** Cadmium forms in alkaline solution a red complex with cadion (1-(4-nitrophenyl)-3-(4-phenylazo)phenyl-triazene). This complex is evaluated photometrically.

(b) **Dithizone method:** Cadmium ions react with dithizone at pH > 6 to form primary cadmium dithizonate, which is stable in a highly alkaline medium and is highly soluble in an organic phase (e.g. carbon tetrachloride or tetrachlorethylene) with pink color. Interfering heavy metals are removed with dithizone in acidic medium before (first extraction in the acidic range). At this pH (pH < 3), cadmium does not form a dithizone complex.

4.2.3.2 Sample preservation

· After adjusting the pH value to 1–2 with nitric acid, the sample can be preserved for storage for up to 1 month (storage vessel: PE or glass bottle).

4.2.3.3 Tips & tricks

Background information

· Only cadmium(II) ions are detected. Decomposition with *NANOCOLOR*® *NanOx* Metal (REF 918 978) or with the decomposition kit (REF 918 08) must be performed prior to analysis for total cadmium determination.

Sea water suitability

· Sea water analysis is possible with the tube test *NANOCOLOR*® Cadmium 2; with the standard test *NANOCOLOR*® Cadmium, it is not. For more information, please refer to the respective instruction leaflet.

pH

· For the cadion method, the pH of the sample solution must be 7–10. If necessary, adjust the pH with nitric acid or sodium hydroxide.

· In the dithizone method, strongly alkaline and strongly buffered sample solutions must be adjusted to pH 3 with nitric acid before measurement.

Interferences

· Various metal ions interfere with the determination by tube and standard tests. The concentration from which on interference is to be expected is specified in the respective instruction leaflets.

· In the standard test, sulfide interferes by producing lower apparent results, and cobalt by forming a brown-violet reaction color (cadmium has a pink reaction color).

· Further interfering ions are listed in the instruction leaflets.

Turbidity

· Turbid solutions must be filtered prior to the determination of dissolved cadmium; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

4.2.4 Chromium

In the environment, chromium is present only in the form of compounds; the most important natural source is chromite ($FeCr_2O_4$). This also serves as starting material for the synthesis of chromium and chromium compounds.

Chromium is the most important alloying element for the production of stainless and heat-resistant steels.

Among other things, chromium is industrially widely used as an alloying element in the field of metal finishing. It is the most important alloying element for the production of stainless and heat-resistant steels. In addition, chromates are used in electroplating (generation of corrosion-resistant chromium coatings), tanneries (suede) and in the paint industry (production of pigment colors).

In industrial wastewaters, trivalent (chromium(III) ions) and hexavalent (chromate and dichromate ions) chromium compounds are found.

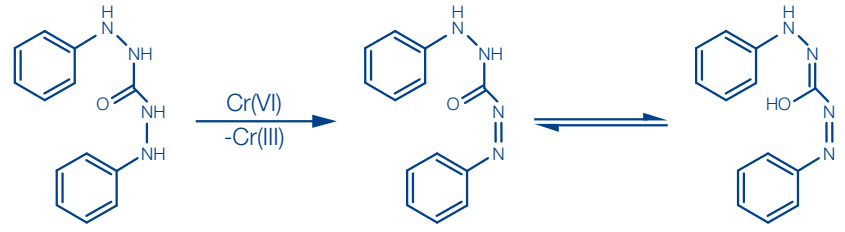
Chromates are toxic and carcinogenic. The toxicity of chromium(VI) ions is much higher than that of the chromium(III) ions. However, chromium and its compounds are essential for humans and play a crucial role in the breakdown of glucose in the blood.

4.2.4.1 Reaction basis

General: For the determination of total chromium, all oxidation states have to be oxidized to Chromium(VI).

Colorimetric and photometric determination is carried out in analogy to APHA 3500-Cr D and DIN 38405-D24.

In sulfuric acid, chromate ions react with diphenylcarbazide to form a purple color. Here, the chromate first oxidizes the diphenylcarbazide(I) to diphenylcarbazone(II). At the same time, chromate (cromium(VI)) is reduced to chromium(III). The enol form of the carbazone forms a purple neutral chelate complex with chromium(III) with the molar ratio of chromium:diphenylcarbazone = 1:1.



Diphenylcarbazide Diphenylcarbazone

4.2.4.2 Sample preservation

· After adjusting the pH with nitric acid to a value of 1–2, the sample can be preserved for storage for up to 1 month (storage vessel: PE or glass bottle).

· Chromate samples must be measured quickly within one day. The sample must be cooled.

4.2.4.3 Tips & tricks

Background information

· Detection of chromium(III) ions requires the prior oxidation to chromium(VI). Without decomposition, only dissolved chromium(VI) compounds are detected. To determine chromium(III), total chromium and chromium(VI) are determined. The difference yields the amount of chromium(III) ions. This calculation can be performed only if there are no insoluble chromium(VI) compounds in the sample solution. These are also determined after decomposition only.

Chromium(III) ions can be determined by differential measurement of dissolved chromium(VI) ions and total chromium.

Sea water suitability

· Almost all *VISOCOLOR*® and *NANOCOLOR*® chromate tests are suitable for sea water analysis. The exception is the standard test *NANOCOLOR*® total Chromium 2 that does not permit sea water analysis. For more information, please refer to the instruction leaflet.

pH

· The sample solution pH values stated in the instruction leaflets must be complied with. If necessary, adjust the pH with nitric acid or sodium hydroxide.

Interferences

· Coloration, turbidity and larger amounts of organic substances as well as oxidizing or reducing substances interfere with the determination of the tube test *NANOCOLOR*® Chromate 5 and the standard test *NANOCOLOR*® Chromate.

· Chloride interferes with the tube test *NANOCOLOR*® total Chromium 2 at concentrations above 1000 mg/L.

· Additional interferences are listed in the respective instruction leaflet.

Turbidity

· Turbid solutions must be filtered prior to the determination of dissolved chromate; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

4.2.5 Iron

With 6.2 %, iron is the 4th most abundant element in the earth's crust and, after aluminum, the second most abundant metal. In water, it is present in various forms. Groundwaters with low oxygen levels and reducing medium often have iron contents of above 0.1 mg/L. The divalent iron(II) Fe^{2+} which is present in those waters is particularly sensitive to air. It is oxidized by atmospheric oxygen to form trivalent iron(III) Fe^{3+}, which precipitates, due to its low solubility, as a brown, fuzzy-amorphous iron oxide hydrate. This oxide hydrate often causes co-precipitation of other heavy metals, due to complex formation, or formation of other iron complexes, especially in waste water and natural waters containing humic acids. Furthermore, the presence of iron is also pH-dependent. At pH values above 8, iron(II) ions Fe^{2+} are converted to poorly soluble iron(II) hydroxides. Dissolved iron can limit the use of the water for consumers, because precipitation can occur upon use of the water, for example in laundering. In industry, iron is used for pipes and containers. Iron in drinking water is undesirable because it leads to brown color and foul odor.

In Germany, the drinking water limit for iron is 0.2 mg/L.

At the usually present concentrations, iron (and manganese) poses no direct health risk to humans. However, in drinking water these compounds are undesirable because they can form deposits in the pipe network that increase the flow resistance to a considerable extent. Consequences of this are firstly unwanted discolorations, on the other hand so-called secondary microbial contaminations due to corresponding iron and manganese bacteria.

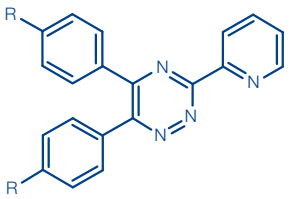
The main application of iron is in the steel and metal industry. Due to its easy availability, strength and toughness, iron is one of the most important base materials. Iron is also used, amongst other things, as a flocculating agent. Determination of dissolved iron is an important indicator of the extent of corrosion.

R = H, SO_3H

4.2.5.1 Reaction basis

Depending on the product range (*VISOCOLOR*® or *NANOCOLOR*®) and test kit, one of two different reactions is underlying:

(a) **Triazine method:** Iron(II) ions react with a triazine derivative to form an intensely colored purple complex (*VISOCOLOR*® and *NANOCOLOR*®).



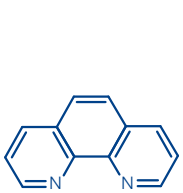
Triazine derivative

Triazine derivatives are highly miscible with thioglycolic acid. Thioglycolic acid is used for the reduction of iron(III) to iron(II), and for pH adjustment. Thus only one reagent is required for analysis.

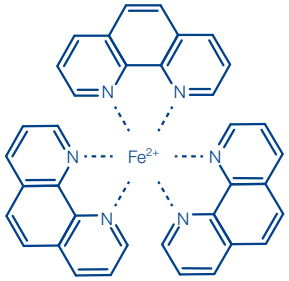
(b) **DIN method:** Iron(II) ions form an orange-colored complex compound with 1,10-phenanthroline (*NANOCOLOR*®).

Iron(III) is reduced by a suitable reducing agent to iron(II) and is also detected. A buffer adjusts the pH.

This orange-red phenanthroline complex is stable in the pH range of 2.5–9. The described method detects dissolved iron and easily soluble iron compounds (underlying reaction in analogy to the german norm DIN 38406-E1).



1,10-phenanthroline



Distinction between total iron and dissolved iron

Dissolved iron comprises only the iron compounds present in the sample in completely dissolved form. Prior to analysis, filtration of the sample with the membrane filtration kit 0.45 µm (REF 916 50) is recommended.

For determination of total iron, decomposition with the reagent *NANOCOLOR*® *NanOx* Metal (REF 918 978) or with the decomposition kit (REF 918 08) is required.

By omission of the reducing agent, Fe^{2+} can be discriminated from Fe^{3+}.

Differentiation of iron(III) and iron(II):

It is possible to distinguish between the two different oxidation states of iron in two tests: *VISOCOLOR*® *ECO* Iron 2 (REF 931 026 / 931 226) and the standard test *NANOCOLOR*® Iron (REF 918 36).

4.2.5.2 Sample preservation

- After adjusting the pH value to 1–2 with nitric acid, the sample can be preserved for storage for up to 1 month (storage vessel: PE or glass bottle).
- After adjusting the pH value to 1-2 with hydrochloric acid 2, iron(II) compounds can be stored for up to 7 days.

4.2.5.3 Tips & tricks

Decomposition

- For the simultaneous detection of iron complexes and determination of total iron, the sample must be oxidatively decomposed with *NANOCOLOR*® *NanOx* Metal (REF 918 978) or the decomposition kit (REF 918 08) prior to analysis.

Background information

· In the determination of iron in aqueous samples it must be noted that the previously mentioned processes will occur after sampling as well. Therefore, differentiated determination of forms present must be done directly on site. If this is not possible, the sample should be stabilized, if possible, by a few drops of acid (use depending on the parameters to be determined).

Filtration

· To determine only "dissolved iron", samples of turbid waters must be filtered prior to analysis.

Sea water suitability

· Almost all *VISOCOLOR*® and *NANOCOLOR*® Iron tests are suitable for sea water analysis. The exception is the test *VISOCOLOR*® HE Iron which does not allow sea water analysis. For more information, please refer to the respective instruction leaflet.

pH

· The pH values which are stated in the instruction leaflets for the sample solution must be complied with. If necessary, adjust the pH with nitric acid or sodium hydroxide.

Interferences

· Oxidants interfere with the determination in the test *NANOCOLOR*® Iron 3

· Other metal ions such as cobalt or nickel disturb the test at various concentrations, depending on the test. The concentration from which on interference is to be expected is specified in the respective instruction leaflets.

· Further interfering ions are listed in the instruction leaflets.

Turbidity

· Turbid samples have to be filtered; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

4.2.6 Copper

Copper is one of the coinage metals.

Copper is, like silver and gold, a coinage metal. The corrosion resistance of the three metals was recognized early, which is why they have been used for production of coins. In nature, copper is found genuine in smaller quantities, but also in compounds such as carbonates, oxides or sulfides.

Copper(II) ions may be present in water in dissolved as well as in insoluble form. In natural waters and municipal wastewaters, copper is normally found only at very low concentrations. In industrial effluents, however, it may be present at significantly higher concentrations, e.g. in metal processing plants, in the electroplating industry and in seepages from waste dumps.

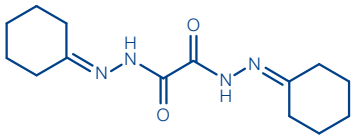
Copper kills germs.

In industry, copper is one of the most commonly used metals. Copper metal is characterized by excellent electrical conductivity, oxidation resistance and thermal conductivity. In addition, it is used in the form of its alloys, such as brass and bronze. Copper has antiseptic effects like silver.

Copper is used, amongst other things, in electroplating plants. Here, the concentration is monitored regularly. It has also been used for water pipes. Depending on the pH value, copper can be detected in drinking water.

4.2.6.1 Reaction basis

Copper(II) ions react with cuprizone (oxalic acid bis-(cyclohexylidene hydrazide)) in weakly alkaline solution to form a blue complex which can be evaluated colorimetrically and photometrically.



Oxalic acid bis-(cyclohexylidene hydrazide)
"Cuprizone"

Cuprizone is very well suited for the photometric determination of small amounts of copper, as it reacts substantially selectively with copper(II) ions.

4.2.6.2 Sample preservation

· After adjusting the pH value to 1–2 with nitric acid, the sample can be preserved for storage for up to 1 month (storage vessel: PE or glass bottle).

4.2.6.3 Tips & tricks

Decomposition

· Only Cu^{2+} ions are detected. Copper(I) compounds and insoluble copper(II) compounds are not detected and must be decomposed before determination. For total copper determination, decomposition with *NANOCOLOR*® *NanOx* Metal (REF 918 978) or with the decomposition kit (REF 918 08) must be performed prior to analysis.

Sea water suitability

· All *VISOCOLOR*® and *NANOCOLOR*® Copper tests are suitable for seawater analysis.

pH

· The pH value which is stated in the instruction leaflets for the sample solution must be complied with.

Interferences

· Calcium interferes with the detection. For disturbance suppression, use the reagent for lime precipitation (up to 20 g/L Ca^{2+}, REF 918 939).

· Chromium(III) concentrations higher than the concentration of copper interfere by causing minor results. For disturbance suppression use *NANOCOLOR*® *NanOx* Metal to oxidize Cr(III) to chromate.

· Further interfering ions are listed in the instruction leaflets.

Turbidity

· Turbid solutions must be filtered prior to the determination of dissolved copper; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

Nickel is the most common cause of contact allergies (nickel dermatitis).

4.2.7 Nickel

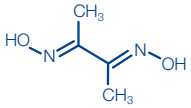
In natural waters, nickel is present only rarely and only in low concentrations. Of greater importance, however, is nickel in wastewater. The nickel compounds contained in water can be present in dissolved (as nickel(II) ions or its complexes) or in insoluble form (e.g. nickel hydroxide, carbonates, sulfides and cyanides).

Nickel is used for metal finishing and for producing corrosion-resistant coatings. As an alloying metal, it is used in steel processing, constituting its main use. Addition of nickel alloys makes steel tougher, more ductile and harder. From the wash water of galvanic plants it can enter the wastewater.

Nickel can cause allergic reactions on the skin. Metal objects that come into contact with the skin are therefore regularly tested for nickel. In the past, many jewelry items (such as earrings) used to be nickel-plated. Due to the high number of people who are sensitized to nickel, fewer and fewer metal items that may come into contact with the skin are nickel-plated.

4.2.7.1 Reaction basis

Colorimetric and photometric determination of nickel ions using dimethylglyoxime (diacetyldioxime).



Diacetyldioxime

4.2.7.2 Sample preservation

· After adjusting the pH value to 1–2 with nitric acid, the sample can be preserved for storage for up to 1 month (storage vessel: PE or glass bottle).

4.2.7.3 Tips & tricks

Decomposition

· Complexed nickel is not or only partially covered analytically and must be decomposed before determination. For total nickel determination, decomposition with *NANOCOLOR*® *NanOx* Metal (REF 918 978) or with the decomposition kit (REF 918 08) must be performed prior to analysis.

Sea water suitability

· Almost all *VISOCOLOR*® and *NANOCOLOR*® Nickel tests are suitable for sea water analysis; some require dilution (1+9). For more information, please refer to the respective instruction leaflet.

pH

· The pH of the sample solution must be 3–8 for the tube tests and 1–13 for the standard tests. If necessary, adjust the pH with nitric acid or sodium hydroxide.

· The pH value which is stated in the instruction leaflets for the sample solution must be complied with.

Interferences

· Calcium interferes with the detection. For disturbance suppression, use reagent for lime precipitation (up to 20 g/L Ca^{2+}, REF 918 939).

· Further interfering ions are listed in the package inserts.

Turbidity

· Turbid solutions must be filtered prior to the determination of dissolved nickel; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

4.2.8 Silver

Silver is one of the coinage metals.

Silver is a soft ductile metal that has the highest electrical conductivity of all the elements and the highest thermal conductivity of all metals. It is a rare element accounting for only about 0.079 ppm of the earth's crust. Like copper, it is one of the coinage metals.

As pure metal, silver is too soft, and therefore it is mainly used in alloys (typically with copper). Like copper, silver has germicidal effects, which is why silver is of interest for medical devices (tablets, ointments, silver foil) as well.

Furthermore, silver is used in photo developing. Fixation is the final process in the development of films and photos. Here, excess silver halides are washed out from the photo layer. Regular control of the silver content of such fixation baths is therefore meaningful and necessary.

4.2.8.1 Reaction basis

Silver ions react with an indicator to form a blue dye. Poorly soluble or complexed silver compounds such as silver bromide, chloride, iodide, cyanide, or thiocyanate are not included in the determination.

4.2.8.2 Sample preservation

· After adjusting the pH value to 1–2 with nitric acid, the sample can be preserved for storage for up to 1 month (storage vessel: PE or glass bottle).

4.2.8.3 Tips & tricks

Decomposition

· Poorly soluble or complexed silver compounds such as silver bromide, silver chloride, silver iodide, silver cyanide or silver thiocyanate are not covered by the determination. For the determination of these compounds, decomposition with *NANOCOLOR*® *NanOx* Metal (REF 918 978) must be performed prior to analysis.

Sea water suitability

· The method is not suitable for the analysis of sea water.

pH

· The pH of the sample must be between 3 and 9. If necessary, adjust the pH with nitric acid or sodium hydroxide.

Interferences

· Various metal ions such as Pb^{2+} or Al^{3+} interfere with the test. The concentration from which on interference is to be expected is specified in the instruction leaflets.

· Further interfering ions are listed in the instruction leaflets.

Performance of the test

· Lower silver concentrations (0.08 to 0.50 mg/L Ag^{+}) can be determined by using 50-mm semi-micro cuvettes (REF 919 50).

Turbidity

· Turbid solutions must be filtered prior to the determination of dissolved silver; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

4.2.9 Zinc

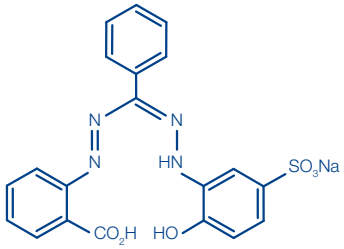
Zinc is an essential trace element.

Zinc is found in many minerals and always bound, mainly in the form of sulfides and oxides. It is an essential trace element for humans, animals and plants.

Zinc salts are used for galvanizing steel (surface treatment) and for the production of zinc alloys. This provides effective rust protection, which is why zinc salts have also been used in some cooling waters. Due to the toxicity of zinc, this is, however, rarely done nowadays.

4.2.9.1 Reaction basis

At a pH of 8.5–9.5, zinc ions form a blue color complex with zincon. The underlying reaction is analog to APHA 3500 Zn-F.



Zincon

4.2.9.2 Sample preservation

· After adjusting the pH value to 1–2 with nitric acid, the sample can be preserved for storage for up to 1 month (storage vessel: PE or glass bottle).

4.2.9.3 Tips & tricks

Decomposition

· For the determination of total zinc, decomposition with *NANOCOLOR*® *NanOx* Metal (REF 918 978) or the crack set (REF 918 08) must be performed prior to analysis.

. Generally a decomposed blank value should be used as reference.

Common sources of error

· When using *VISOCOLOR*® *ECO* Zinc, attention must be paid to the different sample volumes for visual evaluation (1 mL) and photometric evaluation (5 mL).

Sea water suitability

· After dilution (*VISOCOLOR*® *ECO* Zinc 1+9, *NANOCOLOR*® Zinc 4 1+1, *NANOCOLOR*® Zinc 1+9), the method can also be used for analysis of sea water.

pH

· The pH value of the sample solution of 3–10 stated in the instruction leaflets must be complied with. If necessary, adjust the pH with nitric acid or sodium hydroxide.

· For acidic, alkaline and buffered samples, measure pH after adding the sample (target: pH 8.5–9.5) and adjust to pH 9 if necessary.

Interferences

· Calcium interferes with the detection. For disturbance suppression, use the reagent for lime precipitation (up to 20 g/L Ca^{2+}, REF 918 939).

· Further interfering ions are listed in the instruction leaflets.

Turbidity

· Turbid solutions must be filtered prior to the determination of dissolved zinc; turbidity leads to incorrect results: For coarsely dispersed turbidities, use qualitative filter paper (e.g. MN 615), for moderately dispersed turbidities, use glass-fiber paper (e.g. MN 85/70 BF) or membrane filtration set GF/PET 0.45 µm, for finely dispersed turbidities, use membrane filtration kit 0.45 µm or GF/PET 0.45 µm.

Metal analysis with *NANOCOLOR*®

Determination of the total content of metals of heavy metal-containing samples

Homogenisation
for a representative sample

- **Tin** REF 985097, pH 1–7

Digestion
The digestion solution must be clear and colorless. Otherwise additional decomposition is necessary. In case of an insoluble deposit please let it settle down and use only the remaining turbidity-free solution.

- ***NanOx* Metal** REF 918978, 120 °C for 30 min
- **total Chromium 2** REF 985059, pH 1–10, digestion included
- **Crack Set** REF 91808, 100 °C for 1 h

- **Aluminum 07** REF 985098 **, pH 3–6
- **Cadmium 2** REF 985014, pH 7–10
- **Chromate 5** REF 985024, pH 1–7
- **Iron 3** REF 985037, pH 2–12
- **Copper 5** REF 985053 *, pH 1–7
- **Nickel 4** REF 985071 *, pH 3–8
- **Silver 3** REF 985049, pH 3–9
- **Zinc 6** REF 985042 ***, pH 3–10
- **Zinc 4** REF 985096 *, pH 3–10
- **Zirconium 100** REF 985001, pH 0–13
- **Lead 5** REF 985009 ****, pH 3–6

- **Aluminium** REF 91802 **, pH 3–5
- **Cadmium** REF 918131, pH 1–7
- **Chromate** REF 91825, pH 1–9
- **Iron** REF 91836, pH 1–7
- **Iron LR** REF 918128, pH 1–7
- **Copper** REF 91853 *, pH 1–13
- **Nickel** REF 91862 *, pH 1–13
- **Zinc** REF 91895 *, pH 3–10
- **Lead** REF 918101 ****, pH 1–3

Validation of measurement results
More safety by internal quality control

- **Duplicate measurement**
- **Dilution** e. g. 1+99, 1+9, 1+1
- **Standard measurement**
  - *NANOCONTROL* Multistandard Metals 1 REF 925015
  - *NANOCONTROL* Multistandard Metals 2 REF 925016
- **Spiking**
  - *NANOCONTROL* 100 + Addition solution (included in REF 925015 and 925016)

* In the presence of interfering calcium ions, please use the reagent for eliminating lime precipitation (REF 918939).
** Aluminum only with microwave decomposition.
*** In the presence of cadmium ions, please use cadmium compensation reagent (REF 918942).
**** Please refer to the instruction leaflet for further tube and standard tests.

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NANOCOLOR® VARIO C2 M

Digestions for large volumes

Fast, handy, customer-friendly

- Efficient and forward-thinking sample preparation
- Convenient sample digestion
- Only 1 digestion for all metal tests
- Double determination of 4 metal parameters and total chromium at once

4.3 Other important parameters

In addition to wastewater treatment plant and metal parameters, there are other chemical parameters of interest in water and wastewater analysis. The pH is crucial for all chemical and biological processes. But the hardness of the water is also of importance, especially in industry.

Useful background knowledge, information on sample preparation and preservation as well as the underlying reactions for the parameters of hardness and pH are explained below.

4.3.1 Hardness

General hardness or water hardness is defined as the sum of the concentrations of all alkaline earth ions dissolved in an aqueous sample.

$$GH = \sum[Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}]$$

TH = total hardness
Ca^{2+} = calcium ions
Mg^{2+} = magnesium ions
Sr^{2+} = strontium ions
Ba^{2+} = barium ions

However, since, strontium and barium ions are contained only in traces and therefore play only a minor role as hardeners, the definition according to the German norm DIN 38409-H 6 was adopted. According to this standard, the hardness is characterized only by the molar concentrations of calcium and magnesium ions in mmol/L. The amount of calcium ions (Ca^{2+}) is generally higher (about 70–85 %) than that of magnesium ions (Mg^{2+}). The "harder" water is, the higher the total amount of dissolved alkaline earth ions.

Previously, hardness was specified in German hardness degrees rather than in mmol/L (SI unit). This unit referred to calcium oxide (CaO), where 1 °d formally corresponds to 10 mg calciumoxide in 1 liter of water. Other hardness factors such as magnesium were defined equivalently (1 °d = 7.19 mg/L). The conversion of German hardness degrees into SI and other units is listed in the following table:

°d	°e	°f	mg/L CaO	mg/L $CaCO_3$	mmol/L $CaCO_3$
1	1.3	1.8	10	18	0.18
2	2.5	3.6	20	36	0.36
3	3.8	5.4	30	54	0.54
4	5.0	7.1	40	71	0.71
5	6.3	8.9	50	89	0.89
6	7.5	10.7	60	107	1.07
7	8.8	12.5	70	125	1.25
8	10.0	14.3	80	143	1.43
9	11.3	16.1	90	161	1.61
10	12.5	17.8	100	178	1.78

Table 9: Conversion from degrees German hardness into SI and other units

Generally, water with a total hardness of up to 1.25 mmol/L $CaCO_3$ is described as soft, up to 1.98 mmol/L $CaCO_3$ as of intermediate hardness and above 2.16 mmol/L $CaCO_3$ as hard.

Total hardness consists of two differently defined areas:

Carbonate hardness (temporary hardness)

The term carbonate hardness describes the amount of magnesium and calcium ions for which equivalent molar amounts of hydrogen carbonate are available in the solution. In contrast to permanent hardness, the carbonate hardness can be removed simply by heating. This is based on a temperature-dependent equilibrium reaction (carbonate equilibrium):

HCO_3^- = hydrogen carbonate ion
$CaCO_3$ = calcium carbonate ("scale" or "limestone")

$$Ca^{2+} + 2\ HCO_3^- \xrightleftharpoons{\Delta T} CaCO_3 + H_2O + CO_2$$

Limestone ($CaCO_3$) is dissolved, forming calcium hydrogen carbonate, in the presence of carbonated water, which is formed by CO_2 and water. By heating, however, the balance is shifted in the opposite direction, favoring the formation of so-called "boiler scale", calcium carbonate precipitates.

The higher the proportion of dissolved carbonates in the water, the greater the buffer capacity (pH stability) of the water. Very soft waters (e.g. distilled water), however, have a very low buffering capacity, which can affect measurements. By contrast, very hard water leads to a formation of lime and lime soaps, as found frequently in everyday life (kettle, coffee maker). These deposits are formed by the calcium carbonate produced.

The hydrogen carbonates contained in aqueous samples and the good buffer capacity stabilize the pH, even upon introduction of acids and bases:

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \longrightarrow CO_2 + H_2O$$

$$HCO_3^- + OH^- \rightleftharpoons H_2O + CO_3^{2-}$$

HCO_3^- = hydrogen carbonate ion
H_2CO_3 = carbonic acid
CO_2 = carbon dioxide
CO_3^{2-} = carbonate ion

The term carbonate hardness is synonymous with the terms acid capacity or acid neutralizing capacity and alkalinity. The determination is performed by titration with hydrochloric acid against the so-called p value (p = phenolphthalein) and the m value (m = methyl orange).

In the original sense, carbonate hardness was expressed (often in °d) as acid capacity with the unit [mmol/L], or in the fish farming sector as acid binding capacity (ABC) with the unit [meq/L]. This terminology originates from the buffer capacity of the water to acids and the associated pH stability over a certain pH range.

Thus, carbonate hardness, acid capacity and acid neutralizing capacity are homonyms that are merely used in different fields of application.

Carbonate hardness = acid capacity = acid neutralizing capacity

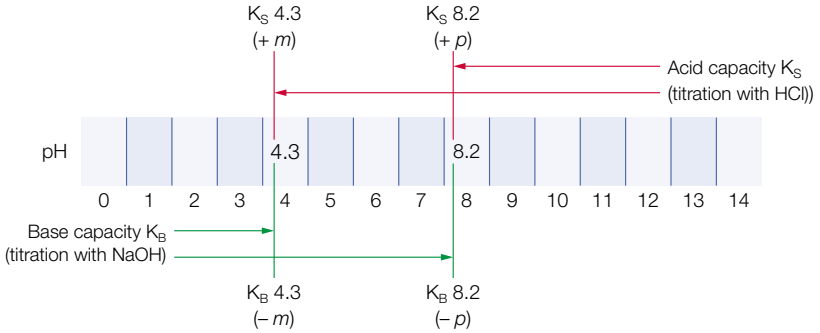
In the first titration stage, the carbonates are converted to hydrogen carbonates. In case of purplish discoloration of the sample after addition of the indicator phenolphthalein, carbonates are present, and titration with hydrochloric acid up to complete decoloration of the sample solution is required. The consumption of hydrochloric acid up to decoloration is referred to as the p value.

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

In the second titration stage, the m value is measured directly after determination of the p value. If after addition of the indicator methyl orange there is a blue color, titration is performed until the color changes to red. All hydrogen carbonates are detected.

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \longrightarrow CO_2 + H_2O$$

Experience shows that in most water samples the p value is very small or zero, since carbonates are poorly soluble. In this case, the carbonate hardness corresponds to the m value.



K_S = acid capacity
K_B = base capacity
HCl = hydrochloric acid
NaOH = sodium hydroxide
m value = carbonate hardness
p value = partial alkalinity

Figure 26: Overview: Acid and base capacity

The carbonate hardness is lower, equal at maximum to the total hardness. However, in exceptional cases it can be greater, namely if more carbonate or hydrogen carbonate ions are present in the sample solution than alkaline earth ions (e.g. in alkali $NaHCO_3$).

Designation	Description	Unit
Total hardness (water hardness)	Concentration of all alkaline earth ions Keywords: Soft water, hard water → lime scale, lime soap	SI: mmol/L
Calcium hardness (calcium carbonate hardness)	Concentration of all dissolved calcium ions	mmol/L often: mg/l $CaCO_3$ or ppm rarely: meq/L
Magnesium hardness	Concentration of all dissolved magnesium ions	mmol/L often: ppm rarely: meq/L
Carbonate hardness (temporary hardness, transient hardness)	Concentration of all alkaline earth ions bound as carbonate or hydrogen carbonate	SI: mmol/L often: ppm rarely: meq/L
Non-carbonate hardness (permanent hardness, sulfate hardness)	Concentration of all alkaline earth ions not bound as carbonate or hydrogen carbonate	SI: mmol/L often: ppm rarely: meq/L
Base capacity KB (Acidity)	Base consumption (NaOH, c = 0.1 mol/L) to reach a pH of 8.2; ability to release protons	mmol/L or: meq/L
Acid capacity KS (acid neutralization capacity from pH 8.3 to pH 4.3)	Acid consumption (HCl, c = 0.1 mol/L) to reach a pH of 4.3, high acid capacity: good buffering capacity, according to: DIN 38409-H7-1-2.	mmol/L or meq/L mg/L $CaCO_3$
Acid-neutralizing capacity (alkalinity)	Ability to bind oxonium ions (H_3O^+) and hydrogen ions (H^+),respectively, depending on basically acting ions, almost only carbonates → "Alkalinity = carbonate alkalinity = carbonate hardness = acid capacity"	mmol/L often: ppm
Total alkalinity	Concentration of all ions that can bind acid (sulfates, phosphates, etc.)	mmol/L often: ppm rarely: meq/L
Carbonate alkalinity	Concentration of all ions present as carbonate that can bind acid. Usually referred to as alkalinity, since carbonates are the main component	mmol/L often: ppm rarely: meq/L

Table 10: Important concepts related to hardness

Non-carbonate hardness (permanent hardness)

Non-carbonate hardness consists of all remaining dissolved, non-precipitable anionic alkaline earth metal salts such as sulfates, chlorides or nitrates. The mole fractions of the individual components do not matter in the determination, since residual hardness is defined as a cumulative parameter and determined as such.

Water hardness is important for sewage treatment plants as well, which is why special softening processes are used.

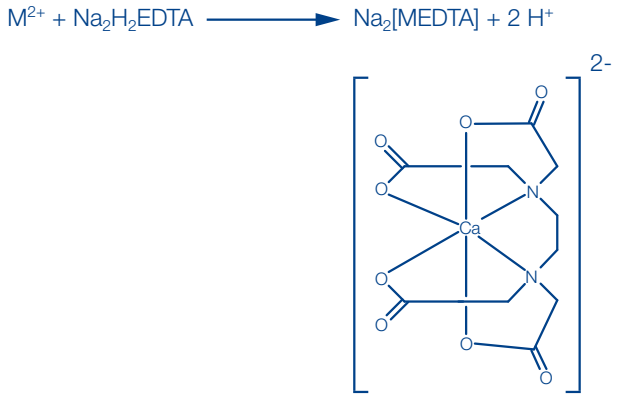
Excessive temporary hardness can lead to deposition of carbonates in the piping and heat exchangers. Too high calcium and magnesium ion concentrations can lead to precipitation of certain anionic parameters.

4.3.1.1 Reaction basis

Total hardness and residual hardness

Depending on the product range (*VISOCOLOR*® or *NANOCOLOR*®) and test kit, one of three different reactions is underlying:

(a) Complexometric titration: Reaction basis in analog to DIN 38406-3 E3
Except for one test kit in the *VISOCOLOR*® range (*VISOCOLOR*® alpha Residual Hardness), total hardness is determined by complexometric titration. The alkaline earth ions are bound by the disodium salt of ethylenediaminetetraacetic acid (EDTA), forming a so-called chelate complex (gr. chele = pincer). While in acid-base titrations (see carbonate hardness) the equivalence point is detected using indicators that respond to a change in pH with a color change, in complexometric titrations metal-specific indicators are used that respond to a change in metal ion concentration. The chelate complexes formed by the indicators with the metal ions differ in color from the free indicators.



The reaction proceeds at a pH of 10. The liquid indicator comprises a buffer substance by which the pH is adjusted and which takes-up the hydrogen ions (protons, +), which are released during titration and which would otherwise lead to lowering of the pH (complex stability decreases with decreasing pH).

In addition to the buffering agent, the indicator composition furthermore comprises Mg-EDTA as complexometrically neutral substance. The calcium complex has a higher stability constant than the corresponding magnesium complex. The result is that calcium ions replace the magnesium ions in the complex and release equivalent amounts of the latter from this complex.

The magnesium ions produce a much sharper color change with the color indicator than the calcium ions. This prevents the problem that in water samples whose hardness is caused exclusively or at least in large part by calcium salts no sharp color change and consequently no accurate endpoint detection of the titration is detected.

Prior to titration, an indicator is added to the water sample. This indicator forms loose complexes of red color with the hardness minerals (alkaline earth ions).

The mixture is then titrated with an EDTA solution, where first the alkaline earth ions not bound to the indicator are converted into chelate complexes. After the binding of these free ions, the ions loosely bound to the indicator are also withdrawn from the complex by EDTA and subsequently chelated.

Due to the decomposition of the indicator/alkaline earth metal ion complexes the indicator changes its color (from red to green) and accordingly indicates the end of the titration. The consumption of titration solution is thus a measure of the concentration of hardness minerals present in solution.

(b) Colorimetry with mixed indicator (only with *VISOCOLOR*® *alpha* Residual Hardness)

(c) Photometric determination of total hardness/residual hardness with phthalein purple. The use of a selective masking agent allows the differentiation of calcium and magnesium in the determination of total hardness.

Chelates complexes are compounds with polydentate ligands which are thus particularly stable.

M^{2+} = metal ion, M^{2+} = Ca^{2+}, Mg^{2+}

EDTA = Ethylenediamine tetraacetic Acid

Carbonate hardness

Determination in the *VISOCOLOR*® range is performed analog to DIN EN ISO 9963-1 C24: The determination is performed by titration with hydrochloric acid against a mixed indicator that changes color at pH = 4.5.

Photometrically, carbonate hardness can be determined using bromophenol blue.

4.3.1.2 Sample preservation

- Total hardness: The sample can be stored after pre-treatment with HNO_3 to a pH of 1–2 for up to one month.
- Carbonate hardness: The measurement must be done within 1 day.
- For storage a PE bottle should be used; store and transport at 4 °C in the dark.

4.3.1.3 Tips & tricks

Background information

- For differentiation of calcium and magnesium contents, a selective masking agent is used for photometric total hardness testing.
- The relationship between water hardness and the magnesium and calcium ion concentrations can be calculated as follows:

Water hardness [mmol/L] ≈ Ca^{2+} [mg/L] / 40 + Mg^{2+} [mg/L] / 24.3 or
°dH ≈ 0.14 · Ca^{2+} [mg/L] + 0.23 · Mg^{2+} [mg/L]

- Normally, carbonate hardness is lower than total hardness. If the carbonate hardness exceeds the total hardness, there is an abnormal situation that requires clarification (e.g. ingress of alkali hydrogen carbonates or high buffering capacity).
- As a screening test for determination of total hardness, AQUADUR® test strips are suitable.

Sea water suitability

- Almost all *VISOCOLOR*® and *NANOCOLOR*® tests are suitable for sea water analysis; some require dilution (1+29). Without dilution, chloride interferences result in incorrect results. For more information, please refer to the respective instruction leaflet. The measurement of residual hardness is not suitable for seawater analysis.

Interferences

- Copper(II) ions may delay the indicator color change (> 5 mg/L) and even completely block it at higher concentrations. Therefore, e.g. sufficient water must be drained prior to sampling with copper pipes. To eliminate copper interferences, the *VISOCOLOR*® *ECO* reagent additive (REF 931 929) can be used for elimination of copper ions in total hardness determination.
- In complexometric titration, the added indicator buffer mixture may be insufficient for a stable pH range around 10 in case of water samples very rich in carbon dioxide or iron. In these cases, dilution of the sample with distilled water (later taking the dilution into account by multiplying the obtained value with the appropriate factor) or addition of additional indicator buffer mixtures must be resorted to. The pH should always be controlled after addition of the indicator buffer mixture for perfect results.
- In the photometric test kits, concentrations above the double measuring range can simulate measured values that lie within the simple measuring range and may thus be misinterpreted. The sample must previously be diluted into the range specified by the test. For water of unknown concentration, studies with strongly differing dilutions should be performed until the last dilution confirms the value previously found.
- Further interfering ions are listed in the package inserts.

Copper(II) ions interfere with determinations. Therefore sufficient water must be allowed to drain from copper pipes.

4.3.2 pH

The pH indicates whether a water or solution is acidic, alkaline or neutral. pH values play an important role in chemistry, engineering, and biological processes. Many chemical reactions, particularly chemical equilibrium reactions, are strongly influenced by the pH. In many such processes, exact determination and appropriate regulation and compliance with the specified pH is required. Thus, e.g. the EC Directive on the Quality of Water Intended for Human Consumption specifies a pH range between 6.5 and 9.5. To achieve such a pH, the water can be treated with commercially available chemicals. Important application areas for pH regulation can be found e.g. in cheese ripening, silage production, tanning, neutralization of waste water, chlorination of swimming pools, paper gluing, lactic acid production, medicine and medical technology, fishkeeping, dyeing processes, preservation processes, cosmetics and many other areas.

Fish, for example, tolerate only a certain pH range in the water. Too low or too high pH values lead to injury to skin and gills. If fish are exposed to such pH values for longer periods of time, this can eventually even lead to death of the animals. The ideal pH range for fish water is generally between 7 and 8.

Normal waters usually have a pH of about 6.5 to 7.5. Domestic sewage is neutral to slightly alkaline, and commercial wastewaters tend to be more acidic, e.g. the pickling waste of the iron working industry.

The definition of the pH is based on the so-called autoprotolysis of pure water. At room temperature, pure water is to a small extent split (dissociated) into equivalent amounts of hydrated hydrogen ions (hydronium ions) H_3O^+ and hydroxide ions OH^-:

$$2\ H_2O \longrightarrow H_3O^+ + OH^-$$

„Autoprotolysis of pure water“

H_2O = water
H_3O^+ = hydronium ion
OH^- = hydroxide ion

The product of the concentrations of H_3O^+ and OH^- is referred to as “ionic product of water” and can be assumed to be an approximately constant value:

$$c(H_3O^+) \cdot c(OH^-) = 10^{-7}\ mol/L \cdot 10^{-7}\ mol/L = 10^{-14}\ mol^2/L^2\ (at\ 25\ °C)$$

Using this ion product, for any given concentration of H_3O^+ ions (from now on referred to as H^+) or OH^- ions the respectively associated unknown concentration can be calculated. According to Brønsted, acids act as H^+ donors and bases as H^+ acceptors. For example, addition of acids to the water increases the concentration of H^+ ions, while that of OH^- ions decreases accordingly. The pH was introduced to simplify the notation of low concentrations and for better comparison.

The pH is thus a measure of the acid or base strength of an aqueous solution. By definition, an aqueous solution is acidic in the pH range < 7 (high H^+ concentration, low OH^- concentration) and basic (alkaline) in the pH range > 7 (low H^+ concentration, high OH^- concentration). A pH of 7 (the so-called neutral point) thus means that the concentration of H^+ ions corresponds to that from the dissociation of pure water (in equilibrium with the OH^- ions).

The pH is a measure of the acid or base strength of an aqueous solution.

Mathematically, the pH (lat.: potentia Hydrogenii) is defined as the negative decadic logarithm of the numerical value of the H^+ activity given in mol/L, and is derived from the ion product (autoprotolysis of water) of water (as a first approximation, the H^+ ion concentration $[H^+]$ can be used in the calculation), so that a numeric scale from 0 to 14 is obtained. The pH is a dimensionless unit.

$$pH = -\log c(H_3O^+)$$

The pH is a dimensionless value.

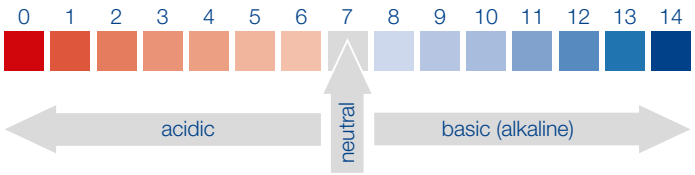


Figure 27: pH value scale

Strong acids and bases, such as hydrochloric acid, HCl, or sodium hydroxide NaOH (caustic soda), are (almost) completely dissociated in solution, i.e. split into their ions. Thus they have a strong influence on the change in concentration of H^+ and OH^- ions, which results in a low (0–3) or high (11–14) pH. Weak acids (e.g. acetic acid, CH_3COOH) and bases (e.g. ammonia, NH_3) are not completely split into their ions in water and therefore affect the pH to a lesser degree.

Salts of weak acids and strong bases (e.g. sodium carbonate, Na_2CO_3) or of weak bases and strong acids (e.g. calcium chloride, $NaHSO_4$) likewise result in pH shifts upwards or downwards, respectively, by hydrolysis (reaction with water / splitting into individual ions). If, however, a salt, such as sodium chloride, NaCl, is dissolved in water, the pH will not change (or only barely), since no new hydrogen ions H^+ are produced or consumed (sodium chloride splits into the ions Na^+ and Cl^-).

pH	Compound
0	36.5 % hydrochloric acid
0.9–1.5	Gastric acid (dil. hydrochloric acid)
2.3	Lemon juice
3.1	Vinegar
2.0-3.0	Coke
4.0	Wine
4.5	Beer
5.0	Coffee
5.5	Tea
6.5	Milk
7	Pure water
7.4	Blood
8.3	Sea water
9.0-10.0	Soap
12.3	Saturated lime water

Table 11: Some examples of average pH values in daily life

The correct pH is an important factor for many detection reactions. The reactions will be affected, if the pH value is not properly adjusted. In most cases, the detection reaction is less selective or does not proceed at all. Such a disturbance may lead to exceedance or undercutting of the permissible monitoring values.

Another important role of pH is in biological wastewater treatment. If the pH of 6.0 to 8.0 is not maintained correctly, the bacteria will die, and the purification cannot be performed.

An excessive pH (above 9) over a longer period in the activation tank leads to increasing ammonia content of the water. Inhibition of nitrification or carbon degradation may result. Too high or too low pH levels can also lead to a decomposition of flakes. Proper separation of filterable precipitates is no longer possible.

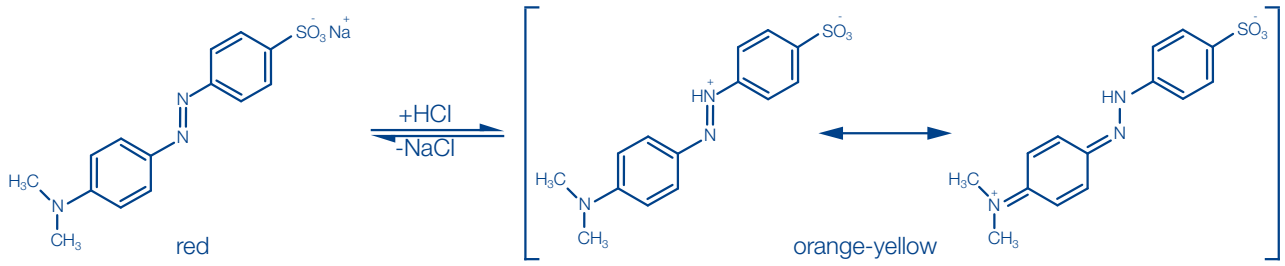
The pH is changed, especially in sewage treatment plants, by entry of certain detergents, toilet cleaners (WC stones) or industrial effluents. The pH should be checked at various stages of degradation.

4.3.2.1 Reaction basis

pH indicator dyes are chemical compounds whose color changes depend on the pH. Most of them are complex organic molecules. Indicator dyes are acids or bases themselves and thus able to release or absorb protons.

pH indicator dyes are chemical compounds whose color changes dependent on the pH.

The color change of the indicators is performed under the influence of the changing concentration of H^+ ions by alteration of the chemical structure, where especially occurrence of quinoid structures or conjugated double bonds is of importance. An example of this is the indicator dye methyl orange, which shows a change in color from red to orange-yellow in the pH range 3.0–4.4.



Methyl orange, sodium salt of 4-[4-dimethylamino]phenylazo]benzenesulfonic acid; pH 3.0–4.4

Indicator dyes belong to various organic dye classes (e.g. azo dyes, phthaleins, sulfophthaleins, benzeines, triphenylmethyl dyes, nitro indicators, etc.). The transition range of the individual indicators extends over 1.2 to 2.5 pH units. Beyond these limits, hue and color depth do not change further.

A special mixture of different indicator dyes shows a characteristic color at any pH. Mixtures of indicator dyes are often referred to as universal indicators, since a combination of appropriate indicators covers large ranges of the pH scale, or even the entire range of 0–14.

Photometric pH determination (*VISOCOLOR*® and *NANOCOLOR*®) takes place in water with phenol red, a triphenylmethane dye, as an indicator. Easy pH measurement is possible with pH indicator strips (pH-Fix).

In strongly acidic media (pH < 1), phenol red shows a red color, at a pH of 1–7.3 a yellow color, while in slightly basic medium (above pH 7.3) the indicator turns purple, and in strongly basic medium (pH > 14) phenol red is colorless. The individual colors are due to the chemical structure.

4.3.2.2 Sample preservation

· The sample should be measured quickly within one day. Long-term preservation is not possible.

4.3.2.3 Tips & tricks

Common sources of error

· Incorrect measurement results due to failure to observe the influence of temperature: The ion product of water is temperature-dependent. The degree of dissociation, i.e. the percentage of dissociated molecules, increases strongly with temperature. All test papers and indicator strips are calibrated to standard solutions of 20 °C.

· pH measurements in colored solutions:
pH measurements in colored solutions always require a special treatment. Theoretically, according to the liquid to be examined, the reference solution should be adjusted to the same color. The same applies to a turbid solution. MACHEREY-NAGEL offers a special form of pH measurement in colored solutions in the form of the PEHANON® indicator papers, where the color comparison scale is subject to the same shifts and influences during the measurement as the comparison field is. Stains and turbidities are thus compensated. Color compensation is also done in the colorimetric *VISOCOLOR*® tests.

· Sources of error that may arise from the contents of the solution to be examined:

1) Acid-base error

- In terms of their chemical nature, acid-base indicators are themselves acids or bases of more or less pronounced character. Consequently, their very addition to non-buffered or only very weakly buffered solutions (e.g. distilled water, neutral salt solutions, solutions of poorly hydrolyzed salts, very weak acids or bases, very dilute solutions of strong acids and salts) will result in a certain change in pH. This error is called acid or base error, respectively, depending on whether the indicator is an acid or a base. These errors are by no means negligible; in the worst cases, these errors can exceed more than one pH unit.
- For this reason, caution is advisable when measuring pH values in non-buffered or weakly buffered solutions.

2) Salt error

- Ions other than hydrogen ions H^+ likewise cause, albeit small, effects on the color development of the indicators. This can lead to color differences in pH measurements in different salt solutions. This effect is known as “salt error”.
  At a salt concentration < 0.2 mol/L, a relevant correction can be neglected.

3) Alcohol error

- When using solvents other than water, the position of the acid-base balance and thus also the indicator constant is changed. This means that in direct color comparison of an indicator in an aqueous buffer solution with a solution containing a small amount of alcohol, identical color does not necessarily imply identical pH values of the two liquids. At room temperature, the alcohol error may be up to 0.5 pH units (indicator-dependent).

Amphoteric compounds may react in one manner or the other, e.g. as acids and bases.

4) Protein error

- Proteins are amphoteric in character, having both acidic and alkaline properties. Thus, proteins bind indicators with acidic as well as with basic character, whereby the resulting color is affected. Thus, pH determination in protein-containing solutions is often very difficult or even impossible. The error is dependent on the type and quantity of the protein, as well as on the nature of the indicator.

5) Alkaloid error

- Alkaloids are also capable of forming conglomerates with certain indicators. If alkaloids are present, it is recommended to perform blank value determinations in order to control the influence of the alkaloids on the measurement.

Background information

· Generally, pure water and neutral salt solutions are very sensitive to atmospheric carbon dioxide. Air contains about 0.03 % v/v of carbon dioxide. In equilibrium with air, distilled water absorbs carbon dioxide. Therefore, under normal conditions distilled water does not exhibit a neutral pH of 7.

· Buffer solutions are required to achieve constant pH adjustment. Buffers are solutions of a weak acid and one of its corresponding salts (e.g. acetic acid / acetate buffer) or a weak base and one of its corresponding salts (phosphate / phosphoric acid buffer). The pH of such solutions will change little or not at all in case of dilutions, or even upon the addition of stronger acids or bases, in the pH range defined for them. It should be noted here that all buffer solutions have a certain maximum buffer capacity. Once this is “used up”, the amount added exceeds the availability of the consumed amount of buffer. For pH measurement using indicator papers, above all adequate buffering is necessary.

Sea water suitability

· All *VISOCOLOR*® and *NANOCOLOR*® pH tests are suitable for seawater analysis.

Interferences

· High contents of neutral salts and colloids as well as organic solvent contents above 10 % can lead to incorrect measurement results (see: “Common sources of error in pH measurements”).

5. Verification of analysis results

By itself, a measurement result is not necessarily correct. Many factors affect the measurement. It is therefore very important to confirm results. The factors that influence measurements and the approaches to ensure measurement results are explained in this chapter.

5.1 Error sources in photometry

In photometry, the concentration of the sample solution is measured with the help of light. The measurement result is the value of the parameter of absorbance, which is obtained by evaluating the measurement. In practice, this method is subject to disturbances. Many of these are due to the nature of the measurement method, but handling and practical performance can also lead to errors.

Errors in analysis are described according to ISO/TS 13530: 2009-03: Water quality – Quality Assurance Guidance for chemical and physico-chemical water testing. All measurement methods in chemical analysis of water and wastewater involve certain errors. This means all measured concentrations can deviate from their actual values.

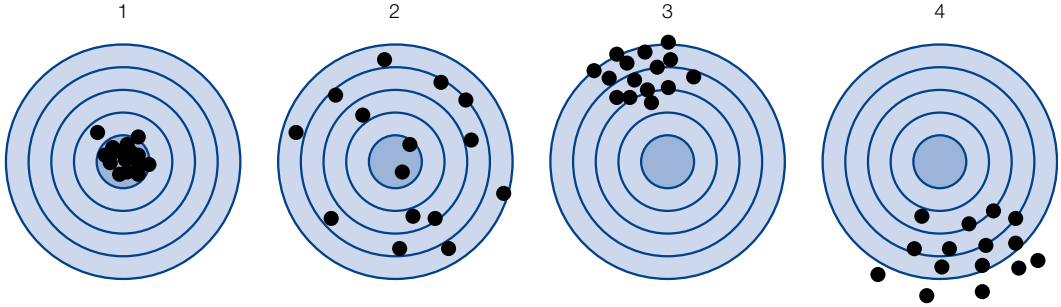
All test procedures are subject to certain errors.

Random errors and systematic errors need to be differentiated.

Random errors are caused by non-influenceable changes during analysis. They vary in magnitude and sign. There is no tendency of the errors recognizable, i.e., for each measurement a different value is obtained. Statistical methods, mostly in the form of error calculations, permit an estimation of errors by calculation. The higher the number of measured values upon which the error calculation is based, the better the estimation can be made.

Systematic errors are present, by contrast, whenever the results show a trend, regardless of whether the test results obtained are higher or lower. Systematic errors occur characteristically during each measurement. Thus, systematic errors cannot be detected simply by repeated measurements. To elucidate systematic errors, a different method of analysis, another instrument or a different sample preparation may be required, depending on the cause of the error

The differences between systematic and random errors as well as the quality parameters of correctness and precision are illustrated in Figure 28.



Error	1	2	3	4
Random	low	high	low	high
Systematic	low	low	high	high
Precision	good	poor	good	poor
Correctness	good	good	poor	poor

Figure 28: Analytical errors

Case 1: All hits are centrally located and close to each other, precision is good. The statistical error is low, the systematic error is zero. The result is correct.
Case 2: The results are scattered around the centre. Precision is poor, but the mean value of the results is correct. The statistical error is high, the systematic error is zero. The result is uncertain.
Case 3: The hits are in close vicinity, but not in the centre. Precision is good, but the result is wrong. The random error is low, the systematic error is high.
Case 4: Hits are widely scattered and displaced in one direction. The result is imprecise and wrong.

A measurement can thus be accurate indeed, but still wrong.

5.1.1 Turbidity

Turbidity (opacity, clouding, haze) is an optical property of a liquid sample describing the degree of clarity. Turbidity is caused by small suspended (insoluble) particles having a refractive index different from the medium. This results in absorption, scattering and reflection of the incident light.

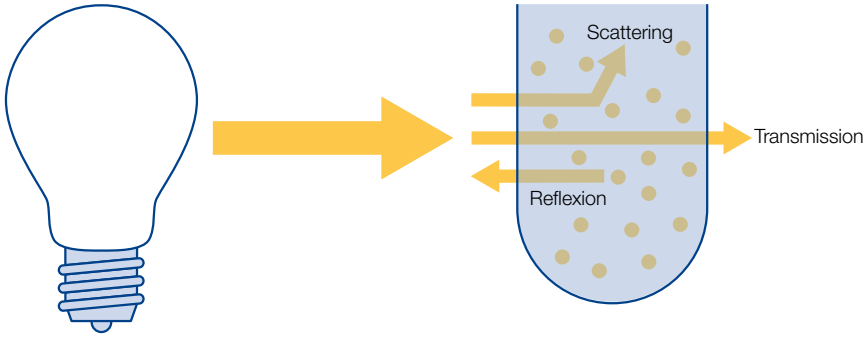


Figure 29: Interaction of light with suspended particles

In general, the higher the turbidity, the more intense is the resulting scattered light. Factors that influence this intensity include the wavelength of the incident light, particle size and shape, the refractive index and color of the sample. Photometry is an objective measurement that allows the comparison of different levels of turbidity. The so-called transmitted light measurement at a measuring angle of 180 ° (absorbance) is recommended In case of heavy turbidity. If there is, however, low turbidity in the sample, measurement at an angle of 90 ° (nephelometric turbidity measurement) is suitable.

In photometry, turbidity is a source of error which is often underestimated. It influences the measured value and is not always easy to identify visually. Even low turbidity, which are imperceptible to the eye, can extremely distort analytical results.

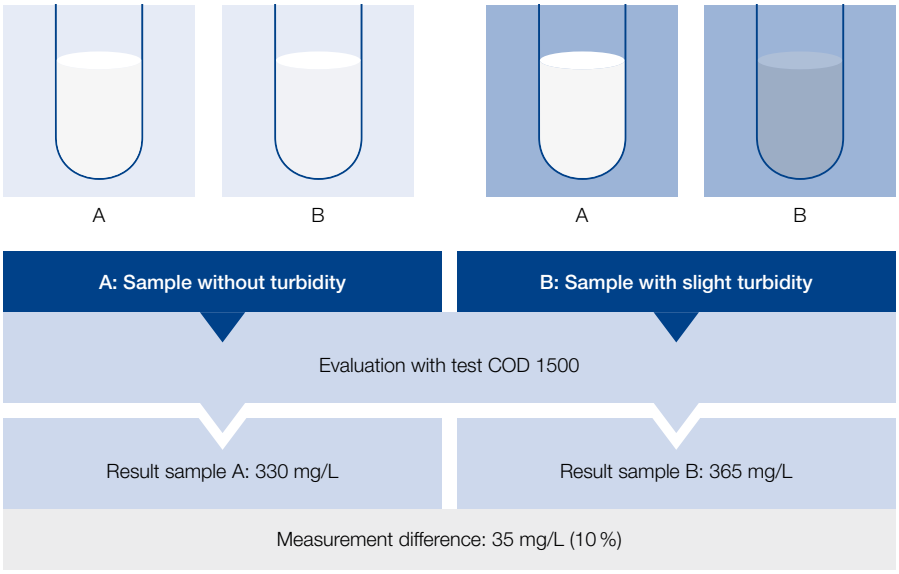


Figure 30: Measurement errors caused by barely visible turbidity in the sample

Whether turbidity leads to higher or lower results, depends on the tube test used, while the measurement error depends on a variety of factors such as wavelength, factor of the test, etc.

Measurement methods

Formazine is usually used as a turbidity standard.

Turbidity can be determined on the one hand by semi-quantitative methods, such as using transparent cylinders or inspection glasses. On the other hand it is also possible to quantitatively detect turbidity using optical measurements.

Measurement methods: nephelometry (scattered light measurement)
Recommended measuring range: 0–40 FNU (DIN EN ISO 7027) Light source and detector are oriented at an angle of 90° relative to each other. The intensity of the light which is scattered by undissolved particles in the sample is measured.

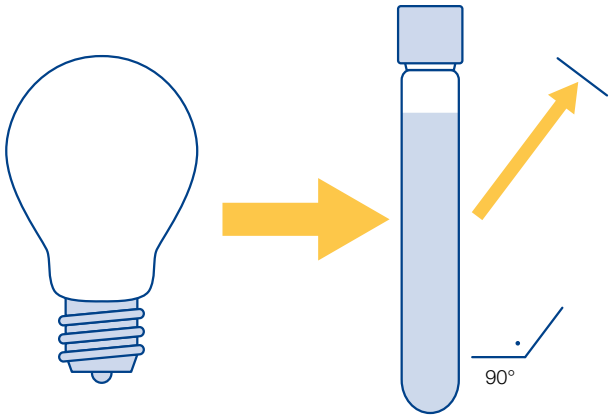


Figure 31: Scattered light measurement

The international unit is the nephelometric turbidity unit, NTU. Other units are FTU (formazine turbidity unit), FNU (formazine nephelometric unit) and TU/F (turbidity unit formazine).

Measurement methods: absorbance measurement (transmitted light or absorption measurement)
Recommended measuring range: 40–4000 FAU (DIN EN ISO 7027) Light source and detector are located on the same axis (180° angle). The reduced light intensity which remains after passing through the sample is measured.

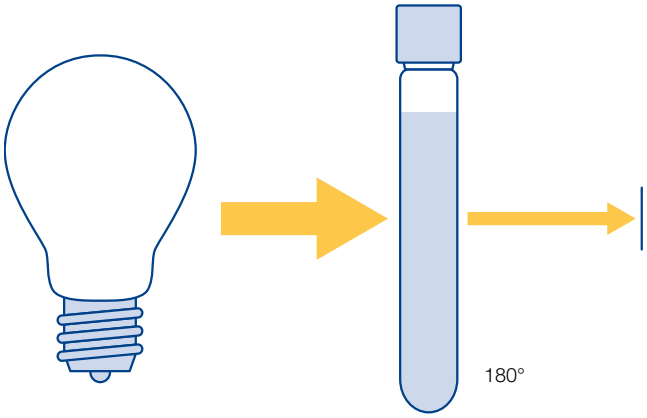


Figure 32: Transmitted light measurement

The international unit is FAU (formazine attenuation unit). In Germany, the spectral absorption coefficient SAK [^{1}/m] is often used.

Selection of the measurement method
Prior knowledge of the particle size or concentration is helpful for correct selection of the measuring method. In general, the following applies:

- Transmitted light measurement at medium to high turbidity concentration (about 40–4000 FAU); used e.g. for determination of the solid portion in activated sludge.
- Light scattering measurement at low turbidity concentration (about 1–40 FNU); e.g. in treated wastewater.

Selection of the wavelength

Turbidity particles absorb at virtually all frequencies, due to their three-dimensional structure. Additional absorption of color in the visible region may be circumvented by a measurement in the infrared (IR) or near-infrared (NIR) range. Accordingly, the attenuation of transmission is a measure of the concentration of turbidity-causing solids. The photometric determination of turbidity is usually done at a wavelength of 860 nm (DIN EN ISO 7027).

Typical turbidity values

Turbidity plays an important role in the assessment of various waters such as drinking water, industrial wastewater and boiler feed water. Turbidity is of particular importance in quality control in the beverage industry, e.g. in the production of fruit juices and beers. In the field of sewage technology, turbidity measurement provides a good opportunity to assess the efficiency of filtering and cleaning. Typical turbidity values are listed in the following table.

Sample turbidity	NTU
Potable water	0.02–0.5
Formazine stock solution	4000
WWTP inflow	70–2000
WWTP outflow	2–40

Table 12: Typical turbidity values

Both scattered light and transmitted light measurements can be used for measuring turbidity with the help of our filter photometers and spectrophotometers.

The transmitted light is measured in 50 mm rectangular cuvettes using filter photometers or spectrophotometers (excepting filter photometer comprising only a round cuvette compartment, such as the compact photometer PF-12^{Plus}).

Photometer	Measurement method	Method number	Turbidity unit [wavelength]
NANOCOLOR® *VIS* *NANOCOLOR*® *UV/VIS* PF-12^{Plus}	Nephelometry	3-07	1–1000 NTU / FNU [λ = 860 nm]
NANOCOLOR® *UV/VIS* II *NANOCOLOR*® *VIS* II	Nephelometry	3-07	0.1–1000 NTU / FNU [λ = 860 nm]
NANOCOLOR® *VIS* *NANOCOLOR*® *UV/VIS* *NANOCOLOR*® *VIS* II *NANOCOLOR*® *UV/VIS* II	Transmitted light measurement	3-05 [50 mm ST]	2–400 FAU [λ = 860 nm]
		3-06 [50 mm ST]	1–100 FAU [λ = 550 nm]
		1-92 [50 mm ST]	1–100 FAU | 0.5–40 ^{1}/m [λ = 620 nm]
		3-10	0–750 mg TSS/L [λ = 860 nm]
NANOCOLOR® 350 D *NANOCOLOR*® 400 D	Transmitted light measurement	1-92 [50 mm ST]	1–100 FAU | 0.5–40 ^{1}/m [λ = 620 nm]
NANOCOLOR® 500 D		3-10	70–750 mg TSS/L [λ = 690 nm]

Table 13: Turbidity measurements with *NANOCOLOR*® photometers

Automatic turbidity measurement for tube tests – NTU-check

The *NANOCOLOR*® spectrophotometers as well as the latest compact photometer PF-12^{Plus} offer the option of automatic turbidity determination. They display of sample turbidity in NTU when performing *NANOCOLOR*® tube tests. With this function, measurement errors due to turbidity of the sample can be detected reliably. Thus, the measurement reliability is increased. If NTU check is enabled, nephelometric turbidity is determined additionally during each tube test.

The NTU value is shown in the display. Measurement value and NTU result are presented in red letters as a visual warning, when an individually adjustable NTU limit is exceeded. The automatic NTU check can be enabled or disabled in the settings (menu) of the photometer.

Which factors influence turbidity?

1) Matrix
   The intensity of the exiting light beam is also affected by particle type and size. To ensure maximum comparability here, turbid samples should be mixed with a magnetic stirrer before measurement.

2) Wavelength
   The general relationship between the measured absorbance of turbid samples and the measurement wavelength is shown in Figure 33. A 50-NTU turbidity standard was used for the wavelength scan.

E = extinction

λ = wavelength [nm]

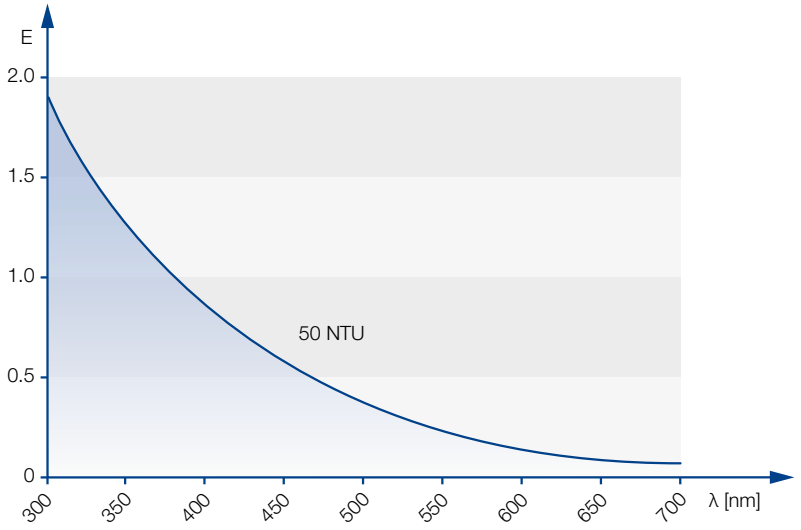


Figure 33: Relationship between wavelength and absorbance at 50 NTU

The absorbance of turbid samples decreases with increasing wavelength. Accordingly different measured values are obtained when measuring a *NANOCOLOR*® tube test at different wavelengths.

3) Factor

In case of turbid samples, the additional particles lead to a measurement error. Depending on the direction of the measurement, this leads to higher or lower results. The extent to which this measurement result deviates from the true value (without turbidity) depends on the wavelength as well as on the respective factor.

The following example illustrates this:
At a wavelength of 620 nm, the turbidity of a COD sample amounts to an additional absorbance of 10 mE. When you evaluate this sample with these two different tests, COD 4000 (Test 0–11) and COD 1500 (Test 0–29), respectively. The following factors are stored for these tests:

Test 0–11 F = 5600
Test 0–29 F = 1740

The concentration of the sample is calculated using the formula

c = concentration

E = absorbance

F = factor

$$c = F \times E$$

The turbidity would thus lead to the following measurement errors in the form of higher apparent results:

Test 0-11 F = 5600 => $\Delta c = 0.01 \times 5600 = + 56.0$ mg/L

Test 0-29 F = 1740 => $\Delta c = 0.01 \times 1740 = + 17.4$ mg/L

The higher the test-specific factor, the larger the measured value deviation.

As a threshold, we recommend a value of 10 NTU for the integrated NTU control function. This ensures maximum safety for all *NANOCOLOR*® tube tests.

Approach in case of turbidity

- Generally, dilutions are an effective tool for reducing the influence of interfering substances and turbidity in any water sample and test. As a matter of principle, the possibility of sample dilution should always be considered. For more information, see section 5.3.3: “Plausibility check by dilution and spiking”, page 93.
- Filtration can be applied prior to determination of non-cumulative parameters. In the determination of cumulative parameters (e.g. COD, total N and total P), filtration is generally not permitted. The process of filtration is explained in more detail in section 5.2.1: Filtration, page 89.
- Correction value determination is required if the turbidity occurs due to reagent addition during the detection reaction, or if the sample must not be pre-treated by filtration (e.g. for cumulative parameters). For more information on correction value calculation, please see section 5.2.2: Correction value, page 89.

In general, all colors and turbidities are destroyed during decompositions when determinations are preceded by decomposition in the heating block. Turbidity remaining e.g. after COD decomposition is mostly attributable to precipitated mercuric chloride. This turbidity can lead to measurement discrepancies in case of too quick measurements. We recommend to wait with the measurement until these particles have settled for values >10 NTU. Excessive chloride concentrations may also lead to finely disperse turbidities in COD determinations, as chloride cannot be sufficiently masked. In this case, another short-term temperature increase causes this turbidity to settle more quickly. We recommend placing the cuvette in the heating block at 50 °C for 1 min.

5.1.1.1 Tips & tricks

Calibration

· The equipment must be calibrated regularly. We recommend performing this quarterly with the help of our *NANOCONTROL* NANOTURB turbidity standards.

Preservation

· Preservation is not possible; turbidity measurements must be made as quickly as possible after sampling. In case of too long waiting times, settling or flocculation of the turbidity-causing particles may occur. This results in distorted readings.

Measuring cuvette

· The cuvette must be free of scratches and fingerprints.

· Depending on the turbidity measurement, the cuvette types must be differentiated. For absorbance measurements, round as well as rectangular cuvettes can be used (180° measurement). For nephelometric turbidity measurement, only round cuvettes can be used (90° measurement).

Interferences

· The sample must be completely free of air bubbles at the time of the turbidity measurement, since otherwise increased measurement results may occur. Air bubbles can be removed e.g. by warming the test sample to about 30 °C or by using an ultrasonic bath.

Conversion factors

· There is no relationship between the turbidity value and the solids concentration in mg/L or ppm. This would require the knowledge of optical properties, size and shape of the suspended solids in the water. Conversion is thus not easily possible.

Assessment of turbidity or coloring

If you are not sure as to whether a disturbing turbidity or color is present, simply carry out a zero calibration of the sample solution against distilled water. In case of turbidity, alternatively the NTU check can be used.

5.1.2 Coloration

Like opacities, colorations have a great impact on photometry. A correct result cannot be obtained if the sample solution already has an intense intrinsic color, or if in the course of the reaction other colors develop due to interfering ions. Colorations may additionally attenuate the light (increased absorbance) and result in deviating measurement values.

For this reason, the sample solution should ideally be prepared in a way that no color is visible anymore. One possibility is oxidative decomposition, in which complexed compounds that are destroyed, which are usually responsible for the color. Information on the decomposition processes which are available for the individual parameters can be found in chapter 4: Important parameters in water and wastewater analysis, page 35 and chapter 3: Decomposition Method, page 27.

A correction value can be used if a decomposition is not possible or desired, e.g. when only the dissolved fraction but not the total content of a parameter in the sample is to be determined,. For more information on correction values please see section 5.2.2 Correction value, page 89.

Colorations attenuate the light and result in deviating measurement values.

5.1.3 Sample preparation

Sample preparation is as important as the subsequent analysis. Correct results cannot be obtained if the sample is improperly preserved (using unsuitable acids or bases, incorrect storage temperature, wrong sample vessel) or prepared (decomposition, filtration). Therefore, check the proper sample preparation mode specifically for each parameter. For more information please see chapter 2: Sampling, preservation and sample preparation, page 19.

5.1.4 Interfering ions

All tests are based on chemical reactions that convert ions into colored complexes. In chemistry, only very few reactions are selective, i.e. undisturbed by other ions.

In practice, ions other than the desired ones react with the reagents to form an analogous complex, a complex of different color, or even inhibit the reaction. Therefore, it is important to know the composition of the sample solution and to pay attention to interfering ions. The interfering ions and their tolerated concentrations are stated in the instruction leaflets.

Dilutions offer the easiest way to avoid disturbances. With every dilution, however, the measurement range of the test kit must be considered. Dilution makes no sense if the measurement range of the test kit is undercut. The concentration of the parameter to be determined must still be within the measurement range, ideally within the middle 20–80 % of the measurement range. All *NANOCOLOR*® photometers are fitted with an integrated dilution calculator to simplify this procedure.

All instruction leaflets can be downloaded for free from ***www.mn-net.com***.

Some interfering ions can be masked or eliminated by an appropriate sample preparation. For example, nitrite, which leads to higher apparent results in the determination of nitrate, can be eliminated by the addition of amidosulfuric acid. Calcium interferences in determination of the metal parameters copper, nickel and zinc can be circumvented using a specific reagent for lime precipitation (REF 918 939).

In the case of the COD tests, the reagent for the masking of chloride ions is already contained in the round cuvettes. However, this reagent can compensate only a certain amount of chloride; In case of larger chloride concentrations, the sample must in turn be pre-treated (e.g. with chloride complexing agent REF 918 911 or cartridges for chloride elimination REF 963 911). Please refer to the respective instruction leaflets for further information.

In addition to interfering ions, the correct pH value must always be complied with!

5.1.5 Homogenization

The analysis of a sample should be as representative as possible. Otherwise, it may happen that only a snapshot at the time and place of sampling is taken. In this case a real statement about the concentration of the parameter cannot be made for the entire sample.

Homogenization of the sample prior to analysis is therefore advisable and mandatory, especially for cumulative parameters. For cumulative parameters, homogenization should be carried out as an integral step in sample preparation using a blender or a so-called disintegrator. Homogenized samples should be analyzed immediately.

For some parameters, however, care must also be taken to ensure that the homogenization does not take too long. Long stirring should be avoided for nitrogen parameters, since this may lead to deviating results (e.g. by expulsion of ammonia from the sample).

5.1.6 Units

The differences between the individual units for one parameter result from the differences in molar masses.

This difference is illustrated using the example of phosphate. The phosphate ion PO_4^{3-} consists of one phosphorus atom and four oxygen atoms. If the unit PO_4^{3-} is used, the concentration of the complete phosphate ion (including the oxygen atoms) is determined.

If, however, PO_4-P is used as unit, only the P portion is used for evaluation, i.e. without the four oxygen atoms. Without the four oxygen atoms, the ion is much lighter, and thus the measurement value is lower. The following Figure 34 illustrates this once more:

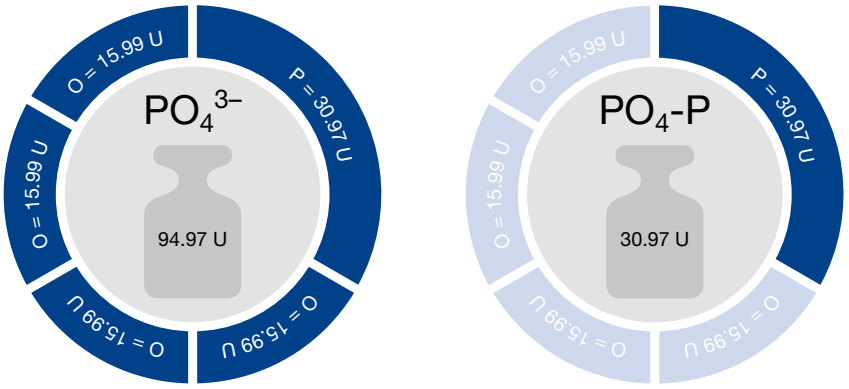


Figure 34: Difference PO_4^{3-} and PO_4-P

U = g/mol

Determination of the conversion factors:

$$\frac{PO_4\text{-P}}{PO_4^{3-}} = \frac{30.97\ U}{94.97\ U} = 0.33 \quad \text{and} \quad \frac{PO_4^{3-}}{PO_4\text{-P}} = \frac{94.97\ U}{30.97\ U} = 3.07$$

For example:

$$1.5\ mg/L\ PO_4^{3-} \times 0.33 = 0.5\ mg/L\ PO_4\text{-P}$$

$$0.5\ mg/L\ PO_4\text{-P} \times 3.07 = 1.5\ mg/L\ PO_4^{3-}$$

You can choose the desired unit in the photometers directly after selecting the test by choosing the corresponding sub-method. Always pay attention to the unit shown in the display in order to avoid possible errors from an incorrect unit. In the photometer manuals and pictograms, all programmed sub-methods are listed for the individual tests.

Factors result from the different masses which permit converting the measured values to the individual dimensions (see Table 14).

Compounds	Conversion		
Ammonium (NH_4^+)	NH_4^+	x 0.78 →	NH_4-N
	NH_4-N	x 1.29 →	NH_4^+
Chromate (CrO_4^{2-})	CrO_{42}-	x 0.45 →	Cr(VI)
	Cr(VI)	x 2.23 →	CrO_4^{2-}
Nitrate (NO_3^-)	NO_3^-	x 0.23 →	NO_3-N
	NO_3-N	x 4.43 →	NO_3^-
Nitrite (NO_2^-)	NO_2^-	x 0.30 →	NO_2-N
	NO_2-N	x 3.28 →	NO_2^-
Phosphate (PO_4^{3-})	PO_4^{3-}	x 0.33 →	PO_4-P
	PO_4^{3-}	x 0.75 →	P_2O_5
	PO_4-P	x 3.07 →	PO_4^{3-}
	PO_4-P	x 2.29 →	P_2O_5
	P_2O_5	x 1.34 →	PO_4^{3-}
	P_2O_5	x 0.44 →	PO_4-P

Table 14: Conversion of chemical forms

5.1.7 Reaction time and temperature

As explained above, in photometry the color of chemical compounds is measured by means of light. Depending on the parameters to be determined and the underlying reaction, different reaction times must be adhered to. The reaction times are stated in the instruction leaflet.

In some cases, the absorbance remains constant after the reaction time, while in others absorption increases further or decreases again. All tests are specifically calibrated for the specified reaction time. If this is not complied with, deviating results are obtained (higher or lower results, depending on whether the absorption continues to increase or decreases). Exceptions are the few tests which absorption remains stable even after a certain time, such as in COD testing.

An overview of the color development of some tests is shown in Figure 35 and Figure 36.

t = time [min]

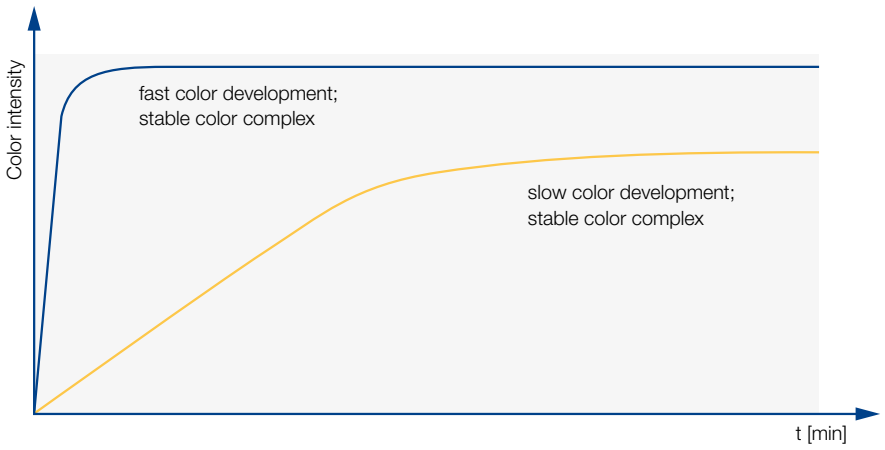


Figure 35: Development of color intensity as a function of reaction time

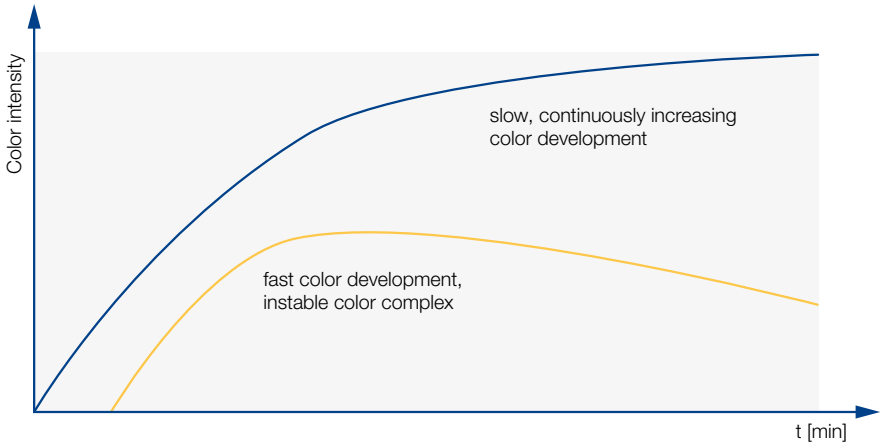


Figure 36: Development of color intensity as a function of reaction time

All tests are calibrated for a specified reaction temperature. In general, the following applies (Arrhenius equation): The higher the reaction temperature, the faster the reaction; and the lower the temperature, the slower the reaction.

If the sample has not the temperature specified in the package insert, this can lead to higher or lower apparent values, depending on the test.

5.1.8 Calibration

All tests are factory-calibrated using standard solutions.

We recommend regular calibration of the photometers (quarterly or semi-annually). The calibration is performed using the supplied calibration cuvette; for exact instructions, please refer to the respective photometer manual.

In addition to the photometers, the pipettes to be used must likewise be tested regularly for their operation, as their calibration often changes over time. The calibration can be done simply by pipetting water and weighing it subsequently. According to the weight, the pipette is then re-adjusted.

The error from incorrectly adjusted pipettes is not to be underestimated, since all tests are adjusted to a specified sample volume. Failure to adhere to the sample volume or proper addition of reagents will lead to significantly deviating results. For more information on pipette calibration, see section 5.3.5: Test Equipment Monitoring, page 97.

We recommend quarterly or semi-annual calibration.

5.1.9 Tests

Testing is an important element in photometry. Only with correct functioning of the test, reliable values can be obtained.

The production of our tests is ISO-certified (EN ISO 9001:2008), ensuring constantly high quality. In addition, all tests are subjected to thorough quality control in our house. However, in rare cases it may happen that a test kit is defective. Therefore, before starting the test always check that the reagents and chemicals are visually in perfect condition (no scratches on the cuvette, leaking chemicals, clumping of solids, etc.).

Please always pay attention to correct storage conditions of the tests. Correct operation cannot be guaranteed in case of incorrect storage. The storage specifications are always listed on the outer label of the package.

All tests have a defined expiration date. After this date, as well as after incorrect storage, correct functioning cannot be guaranteed anymore.

The reactivity of the test can be checked by a measurement of a standard in case of doubt.

The EN ISO 9001:2008 certification ensures consistently high quality.

5.1.10 Cleanliness

Clean work is essential for correct results in analytics. Attention should always be paid to a tidy workplace and cleaned equipment. In case of contamination, the cuvette compartment can be cleaned with a soft cloth and water or isopropanol. Please do not use abrasive cleaners.

Before measuring, each cuvette should be wiped clean with a cloth. Fingerprints and soiling affect the beam path and lead to deviating results.

The pipette tip must be clean. Replace it before adding different reagents, or if you want to perform different parameters. Carryover of interfering ions can happen very easily and is often underestimated.

A typical example is the parallel analysis of phosphate and nitrate, two major sewage treatment parameters. The same pipette tip is often used to pipette the sample solution first into the nitrate cuvette and then into the phosphate cuvette. Even the slightest touch of the pipette tip at the top edge of the nitrate cuvette, leads to deviating results in the determination of phosphate. The nitrate tube contains phosphoric acid, which due to its viscosity creeps upwards on the glass wall and thus reaches the pipette tip.

For each parameter and each reagent, the pipette tip should be changed.

5.1.11 Test performance

The operator's way of working of the test performance is also a crucial criterion for correct analysis results. Reliable results cannot be obtained even if all the requirements listed above have been met, but the test is performed incorrectly.

Therefore, always make sure that all steps have been carried out in the correct order, and that all times and sample or reagent additions have been made correctly.

Correct handling of the pipettes (pressure point, bubbles in the pipette tip) and use of the equipment must likewise be ensured.

A critical questioning of one's own way of working is essential in order to ensure correct results.

The own working method can be checked quickly and easily at any time by standard measurements. Further information about verification of the analysis results can be found in section 5.3 Internal Quality Control According to DWA-A 704, page 90.

Possible errors in photometry

Errors in analysis preparation and performance	Errors in the handling of the equipment	Errors from additive disturbances	Errors from proportional disturbances
· Errors in sampling (homogenization, sampling equipment, location, etc.) · Failure to pay attention to turbidity, intrinsic color, possibly required filtrations · Imprecision in the addition of reagents, in the preparation of dilutions and corrective values, carryover of sample solution · Failure to observe the prescribed pH, strong buffer concentrations · Too vigorous shaking of reagents · Selection of incorrect dimension · No-compliance with interference limit concentrations · Failure to pay attention to precipitations · Improper preservation of samples · Measurements at the limits of the measurement range · Errors in the decomposition of the sample solution	· Derivation from the analytic procedure (reaction time, temperature, blank value, factor, pH) · Imprecise pipetting (pressure point, adjustment, air bubbles, wet tips) · Impurities (glass equipment, fingerprints, dust, smoke) · Use of an incorrect blank solution (other batch) · Use of overlaid tests, incorrect storage · Multiple use of the same pipette tip · Wrong calibration of the photometer (contaminated solution / measurement cuvette)	· Other substances in the buffer solution likewise produce a color reaction · The test solution is colored or turbid (corrective value necessary) · A part of the substance of interest is not accessible to analysis; it is present in particulate form or is bound in a complex or by adsorption (decomposition is required) · Possible detection by determination of a corrective value! Cannot be detected by standard addition!	· Other substances suppress or enhance the detection reaction · High concentrations of acid, alkali or buffer prevent the correct adjustment of the pH necessary for the reaction · Competitive reactions of interfering substances lead to lower apparent findings · Incorrect sample or reagent volume (defective pipette) · Possible control by standard addition with *NANOCONTROL*

Figure 37: Possible errors in photometry

5.2 How to deal with interferences

For the removal of any existing interference and ensuring reliable analytics, various methods such as filtration or a correction value can be used.

5.2.1 Filtration

Filtration can be performed prior to determination of individual parameters. In the determination of cumulative parameters (e.g. COD, total N and total P), filtration is generally not permitted.

Filtration is a mechanical separation process for the separation or purification of a medium. In filtration, the sample solution to be separated passes through a filter that is individually matched to the test solution.

Filtration is a mechanical separation process for the separation or purification of a medium.

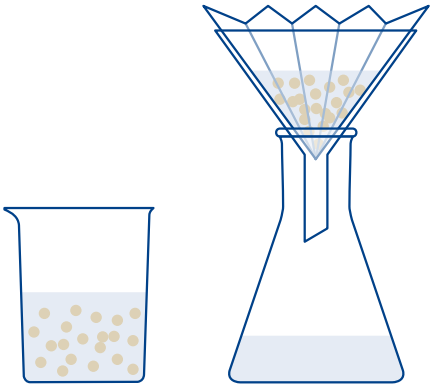


Figure 38: Filtration

Various filter materials are available. Most commonly, paper filters are used; furthermore glass fiber filters, quartz fiber filters, metal filters or membrane filters are applied. It is important to always use a filter which is appropriate for the application.

Filter papers are characterized by parameters such as weight per square meter, thickness and filtration speed; for membranes, the manufacturing process permits specifying a precise pore size.

Paper filters are available as round or pleated filters, as qualitative or ashless quantitative papers. Glass fiber filters are characterized by elevated temperature stability and high filtration speeds despite high retention capacity compared to paper filters.

Pre-filtration of the sample is helpful in case of the presence of intense turbidity, if only solutes are to be determined. The choice of the right filter depends on the degree of turbidity or size of the particles.

Fine-particle turbidities:

· With membrane filtration kit 0.45 µm
· With membrane filtration kit GF / PET 0.45 µm

Intermediate-particle turbidities:

· With glass fiber paper, e.g. MN 85/90 B
· Membrane filtration kit GF / PET 0.45 µm

Coarse-particle opacities:

· Using qualitative filter paper, e.g. MN 615.
  If necessary, carry out a fine filtration with a 0.45-µm syringe filter.

5.2.2 Correction value

Turbidity and coloration additionally attenuate the light and lead to increased absorbance.

A correction value can be used if decomposition is not possible or desired (e.g. in the determination of dissolved substances).

For combined parameters where no pre-filtration is allowed by definition, a correction value is a viable option.

The correction values require a special approach for each test.

The correction values require a special approach for each test. For example, it is not sufficient to simply measure the intrinsic color of the sample without reagents and subtract it from the measured value. In many cases the reagents change the color or turbidity of the sample. All changes of the sample, such as dilution, addition of chemicals affecting pH or redox potential, must reflect those of the original analysis. Only the main reagent, which forms the dye required for the analysis, is not added.

Basic approach:

Determine value according to original procedure = A

Determine correction value according to special procedure = B

Analysis value = A – B

Exceptions: Methods where decreasing extinctions are measured against a reagent blank value. Then the following applies: Analysis value = A + B. This is stated in the instruction leaflets of the according tests

It is very important that only values of the same dimension are subtracted from each other (e.g. mg/L N; mg/L NH_4; mmol/m^3; E).

If the correction factor for several samples in the same matrix is so low that it is negligible for the current measurement problem, it can be ignored. However, this can be found out only from practical testing and is not evident before!

The methods for determining the correction values for the individual tests and the cases in which exceptions are to be made are explained in the respective photometer manual.

The aspiration of a photometric analysis to accuracy requires that only the light attenuation is measured which is caused by the reaction color of the relevant substance / color complex. Light attenuations due to filter, cuvette or reagents in the form of intrinsic color or turbidity must be compensated.

Exactly this is the purpose of so-called blank values. With a blank solution, the photometer is set to a baseline value. Zero values may be:

a) sample solution without reagents

b) sample solution with several reagents

c) distilled water with all reagents

d) a zero solution enclosed with the reagent set and produced specifically for this batch

In the *NANOCOLOR*® photometers, the zero values for almost all cuvette tests are pre-programmed. For some tests, however, the blanks must be adjusted for each batch separately.

Difference between zero value and correction value:

Zero values compensate all reaction-specific influences, while correction values compensate sample-specific influences.

Zero values compensate all reaction-specific influences, while correction values compensate sample-specific influences.

5.3 Internal quality control

Operating methods are an accepted form for plant control and monitoring. The fast information is a fundamental advantage of these methods compared to standardized analytical methods with high expenditures in terms of time and instrumentation. Further advantages include a lower need for reagents, low cost and swift performance.

Use of operating methods can significantly reduce the use of reference methods. Many official regulations consider operational analytics as a key function in plant monitoring.

In the selection of operating methods, the expected result should be in the mid-range of the assay, in the so-called 20–80 % range; dilution steps to enter this range are permitted.

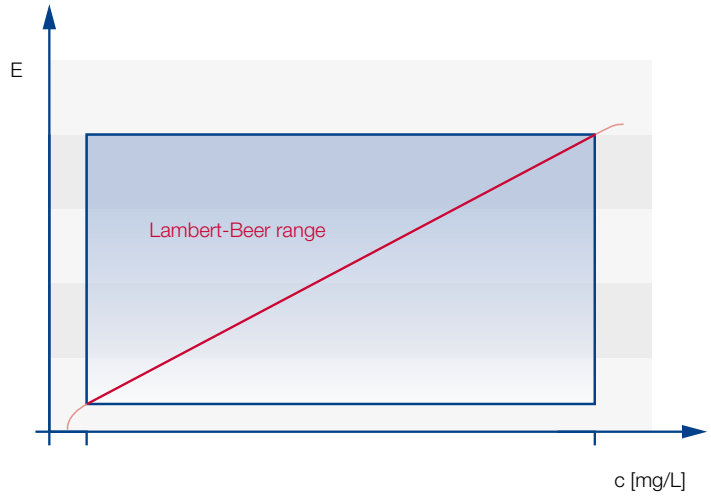


Figure 39: Diagram for the Lambert-Beer law

E = extinction
c = concentration [mg/L]

There is less scattering within the 20–80 % measurement range while reliability is highest. This is illustrated in Figure 39. Internal quality control (IQC) is a crucial aspect with increasing importance in every laboratory.

All components of an analysis system, such as reagents and tests, measuring equipment and personal handling, must be regularly monitored and tested in most laboratories. This is important to ensure correct results and to meet validation requirements.

There are various internal and external options for checking the analysis system as well as one's own work.

Consistent implementation of documentation in the fields of test results, quality control and qualification provides objective proof of the quality of the analyses and the measurement results. Analytical quality assurance and documentation are of equal importance. Only by proper documentation, proof can be furnished as to when and by whom which measurements were carried out, whom controlled this activity, and which level was reached in operational analytics.

In the following part, some important measures of analytical quality assurance will be presented. It must be emphasized that a single measure of IQC may not be enough, so ideally the full range of quality assurance measures should be applied.

5.3.1 Multiple determinations

Multiple determination of an existing sample is the easiest way to ensure the precision of a reading. Repetition of individual crucial steps such as sampling, filtration or decomposition is also possible.

Multiple determination is the easiest way to ensure the precision of a reading.

The advantage of multiple determinations is that outliers are detected immediately, or at least the trend or dispersion of the development of the measured values is visible. Frequently e.g. a duplicate determination or a triplicate determination is performed in order not to waste valuable time, e.g. by decomposition.

Multiple determinations should be done regularly even with familiar samples, but are mandatory for unknown samples and important measurements.

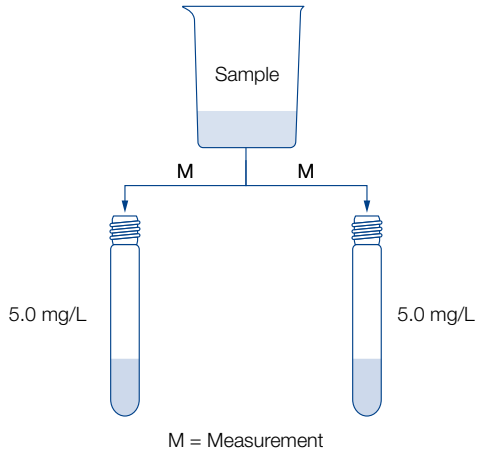


Figure 40: Principle of multiple determination

5.3.2 Standard measurements

For a standard measurement, a standard solution of known concentration is used instead of the real sample.

By standard measurements, the entire analytical system can be checked.

The principle of a standard measurement is simple: Instead of the actual sample, a standard solution of the parameter with a known concentration is used. The test is performed as usual according to the instructions on the instruction leaflets.

If the correct value is reached – differences within the confidence interval can be tolerated here –, then all the individual components of the analysis system work properly. The own working methods can thus be controlled in this way as well. Ideally, the specified value is achieved precisely.

However, when using standard solutions it must be taken into account that they do not comprise any interfering substances. The real sample may therefore still cause problems in analysis.

By now, for most parameters ready-to-use standard solutions are commercially available. When working with standard solutions, it is always important to ensure that the concentration of the standard solution is appropriate for the measuring range, or to prepare any dilution that may be necessary prior to use. In principle, standards can be prepared internally from suitable compounds.

The correct preparation, the concentration of the measuring range and the storage conditions of the standard solutions must be ensured.

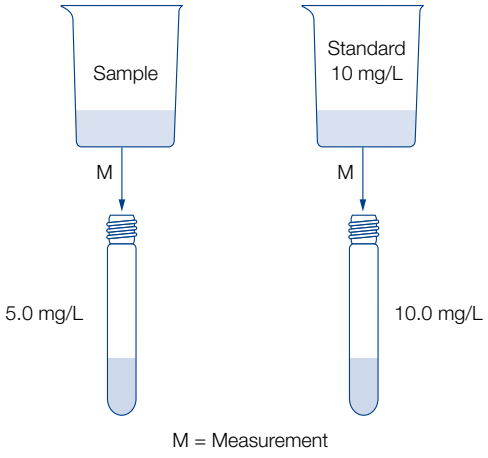


Figure 41: Principle of standard measurement

NANOCONTROL Standards

Maximal control of your results

Analytical quality control

- Defined concentration of a particular substance
- Control of the complete analytical system in accordance to DWA-A 704
- Broad range of products for special applications

5.3.3 Plausibility check by dilution and spiking

Dilutions are an effective tool for verifying results and reducing the influence of interfering substances and turbidity in all water samples and tests. Dilutions are used whenever the measuring range is exceeded, when general doubts about the accuracy of the analytical results occur, or when interfering ions or turbidity in the sample solution exist that influence the outcome. Dilutions are often used merely to verify the results.

As a matter of principle, the possibility of sample dilution should always be considered.

For dilution, normally distilled water is used. Exceptions are the parameters COD (chemical oxygen demand), for which determination COD free water is used, and silica, for which the sample is diluted with silica-free water.

After dilution, the expected reading should ideally be in the middle of the measuring range, the so-called 20–80 % measurement range, and definitely not outside the range. If the measured value should be outside the measuring range, a test with a smaller measurement range or a lower dilution must be selected.

For convenience, all *NANOCOLOR*® photometers are fitted with an integrated dilution calculator.

Distilled water, COD-free or silica-free water is used for dilution.

Dilutions are entered into the photometer in the form 1 part of sample + x parts of distilled water

e. g. 1+9 (dilution 1:10)
1+24 (dilution 1:25)
1+99 (dilution 1:100)

Depending on the sample volume, the dilution can be prepared in a 100 mL volumetric flask, or directly in the cuvette. The following tables give an overview of various dilutions depending on sample volumes.

mL Water sample	mL distilled water	Multiply measurement result (and range) by
50	50	2
25	75	4
10	90	10
5	95	20
2	98	50
1	99	100

Table 15: In the 100 mL flask at 0.2–1.0–2.0–4.0 mL sample volumes

mL Water sample	mL distilled water	Multiply measurement result (and range) by
10	10	2
5	15	4
2	18	10
1	19	20
0.5	19.5	40
0.2	19.8	100

Table 16: For 20 mL sample volumes (prepare directly in the volumetric flask)

mL Water sample	mL distilled water	Multiply measurement result (and range) by
25	25	2
10	40	5
5	45	10
2.5	47.5	20
1	49	50
0.5	49.5	100

Table 17: For 50 mL sample volumes (prepare directly in the volumetric flask)

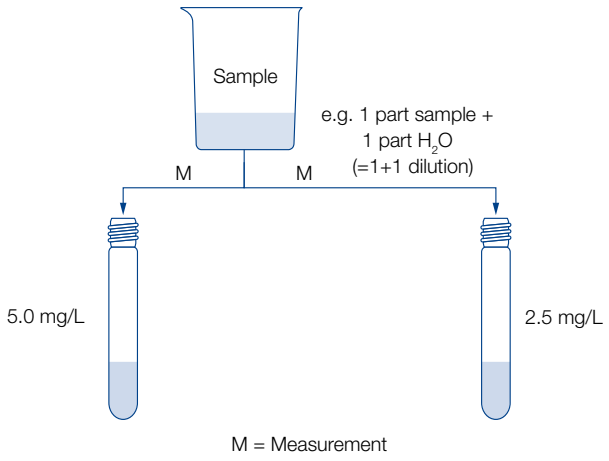


Figure 42: Principle of dilution

Just as the concentration of a sample can be diluted, the concentration of one or more parameters can be increased. This is called addition or spiking.

It is crucial that a known concentration of the parameter to be determined is added to the actual sample, and then precisely this increase is recovered. The recovery rate is determined by measurement prior to the addition and measurement following the addition. With the number of addition steps, the reliability of the measurement increases.

After a standard addition, three different results can be obtained:

1) The increases in concentration equal the value of the addition; no proportional error has occurred.
2) The concentration increases are disproportionately higher or lower. This may indicate matrix interference. Further investigations of the sample solution are advisable in this case; for example, contents may react in a manner similar to the respective analyte, or contents may mask the parameters.
3) The concentration increases differ strongly from each other, sometimes above and sometimes below the expected value. In these rare cases, there are disproportionate interferences, which may be due to faulty sample preparation.

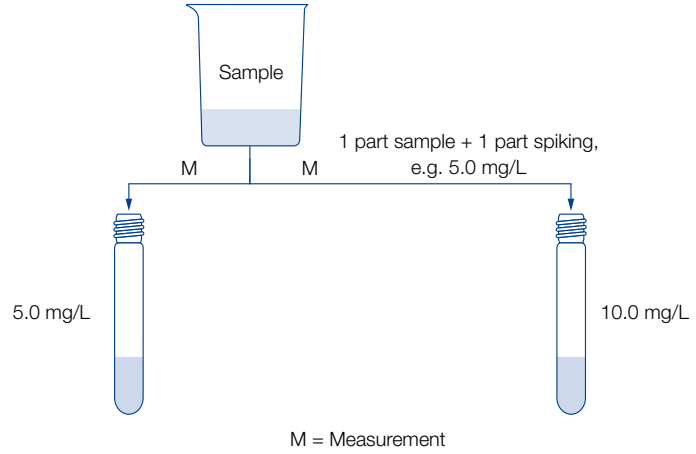


Figure 43: Principle of spiking

There is additionally the possibility of performing the spiking directly into the sample tube when testing with a sample volume ≥ 2.0 mL, (20 µL of spiking solution to 2 mL sample volume, 40 µL of spiking solution to 4 mL sample volume, etc.)

By spiking, matrix effects that impact the analysis can be identified very easily. Such matrix effects may e.g. occur due to complexing agents or ions that react with the substance to be determined to form poorly soluble substances, making the parameters inaccessible to analysis.

If a spiking is not recovered, further sample preparation and analyses concerning the nature of the sample should be made. Furthermore, it is possible to calculate the probably correct analysis value. The method for calculating the probable analysis value by use of a standard spiking is illustrated in Figure 44.

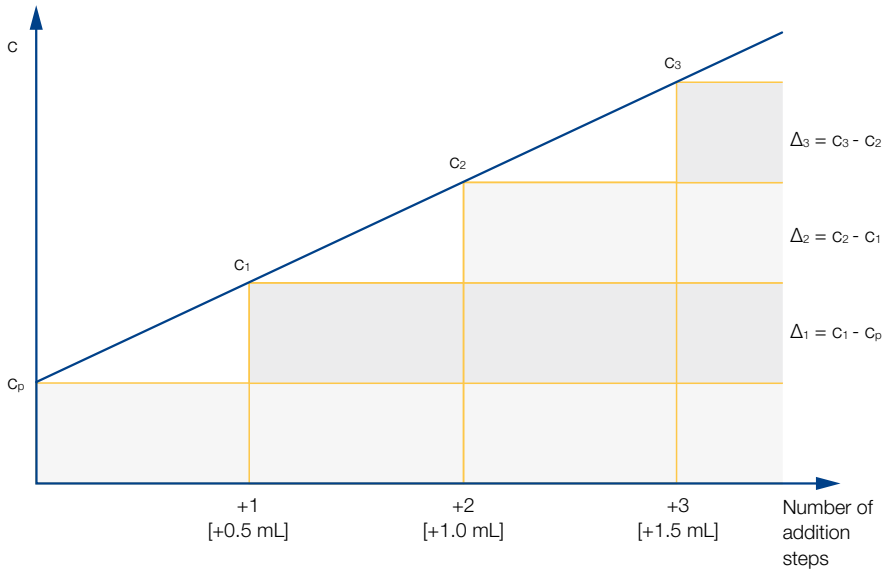


Figure 44: Evaluation of a standard spiking

c_P = concentration of the original sample

c_{1-3} = concentration after addition of spiking solution

Δ_{1-3} = concentration difference

5.3.4 Parallel measurements

For parallel measurements usually the operating method is compared with the corresponding reference method in a contract laboratory. Those parallel measurements permit direct comparison of the sample solution for each parameter.

The requirement for such a parallel measurement is that the measurement is performed by applying both methods to the same, split sample. In most cases the sampling and splitting of the sample are carried out by the reference laboratory. The subsequent sample preparation and / or preservation should be coordinated with the laboratory in order to avoid errors or discrepancies. Due to the potential danger of changes to the sample, analyses should be carried out as quickly as possible and from all sampling points relevant for the operator.

Measurement results should always be backed by duplicate determinations and plausibility checks.

c = Concentration [mg/L]
CI = Confidence interval
Target = Target value

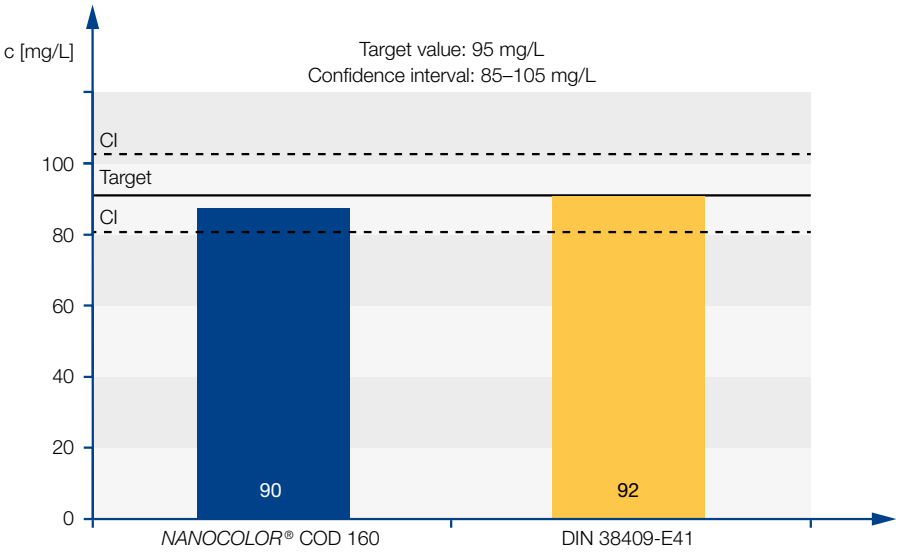


Figure 45: Comparability *NANOCOLOR*® and DIN

c = Concentration [mg/L]
CI = Confidence interval
Target = Target value

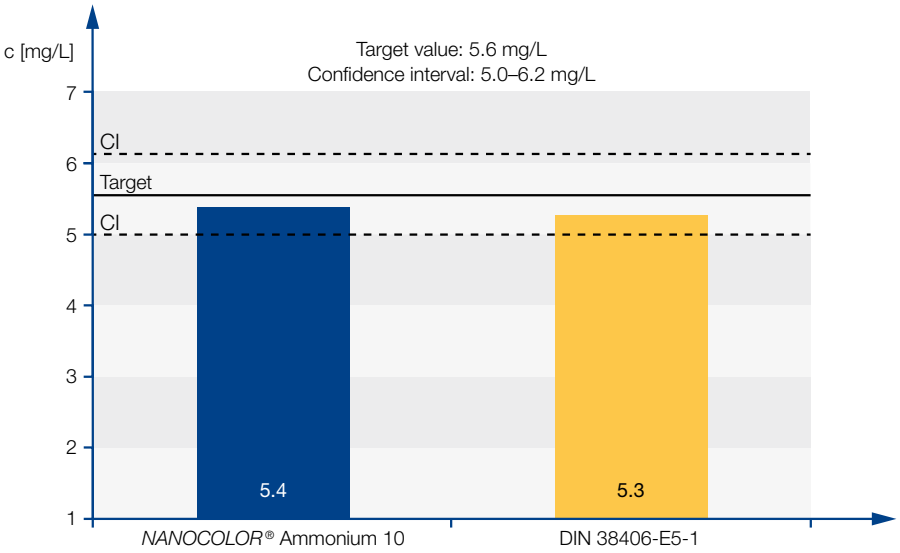


Figure 46: Comparability *NANOCOLOR*® and DIN

5.3.5 Test equipment monitoring

The term test equipment covers any devices and reagents used in operational analytics, such as photometers, heating blocks, pipettes and balances.

Only if the equipment is constantly checked, you can be sure that it meets the required and necessary working conditions. Equipment not properly tested may directly or indirectly cause false readings. Incorrect measurements can have various causes, for example incorrectly calibrated pipettes, impurities in the cuvette compartment or insufficient decomposition in the determination of cumulative parameters.

Photometer

Certainly the most important aspect among the test equipment is the photometer. Without photometer, no analysis can be performed. It is suggested to perform the control semi-annually according to the manufacturer's instructions and in a device-dependent manner. The crucial question should always be: "Can I rely on the readings under the assumption that all other factors affecting the measured value were tested and do not cause errors?"

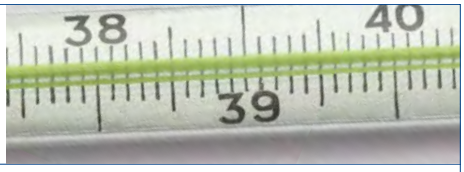
The accuracy of the photometer is often checked by the manufacturer itself, and a corresponding report is carried out. However, under certain conditions the testing can be performed independently. The advantage of independent control is that it can be individually integrated into everyday operations. It is crucial that the users themselves do not influence the review, possibly alter the results, but can nevertheless accomplish performance in the simplest manner (e.g. without opening the device).

Heating blocks

Heating blocks or heaters should be tested annually for the reaction temperature. Complete decomposition can be guaranteed only when the reaction temperature is correct. The deviation of the decomposition temperature should not exceed ± 3 °C.

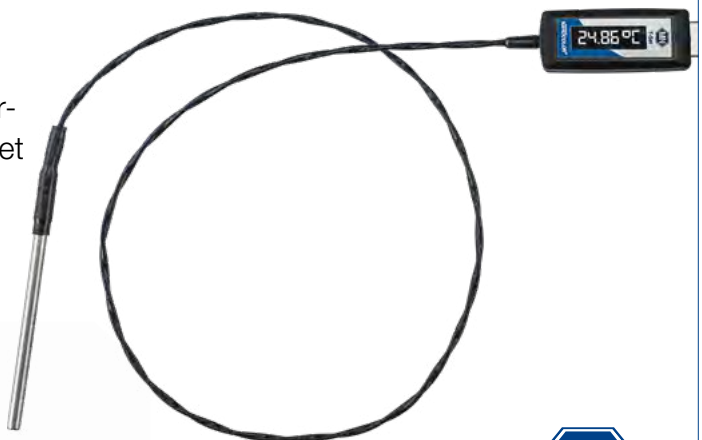
Specially calibrated, external temperature sensors or thermometers are used for control. As with the photometers, the testing is usually managed by the manufacturer of the devices. However, here, too, independent verification of the equipment is possible. As already mentioned for the photometer, the advantage of independent control is that it can be individually integrated into everyday operations. To monitor the heating blocks, the *NANOCOLOR*® T-Set, a calibrated thermos-probe, can be used.

NANOCOLOR® T-Set
Heating block monitoring



Temperature control and calibration

- Calibrated thermal sensor for automatic temperature control
- Automatic calibration of all *NANOCOLOR*® heating blocks
- Easy creation of quality certificates in accordance to GLP with the *NANOCOLOR*® T-Set software



Pipettes

Operational analyses are in most cases performed by photometric testing. Inaccurate pipettes are a major source of mistakes. Pipettes are precision instruments crucial for reading accuracy and therefore must be checked as regularly as photometers or heating blocks. A scale with an accuracy of 0.01 g meets all the requirements for testing and calibration of pipettes used in photometry. It is recommended to separately check the volumes used most frequently.

· The smaller the receiving volume of a pipette, the more sensitive it is. Digital piston pipettes have a mechanical adjustment mechanism. These pipettes are to be treated with special care, since overwinding the setting can cause serious damage.

Calibration notes:

- The pipette should be checked quarterly. If accidentally liquid should have entered the pipette, the latter must immediately be cleaned thoroughly, controlled and if necessary recalibrated.
- Each pipette comprises functional sealing elements that age. Spare parts should be available in due time.
- Test conditions (see also DIN 12650, part 6): Room temperature 20–25 °C, calibrated scale with corresponding display accuracy of 1/100 g. As test liquid, distilled water tempered to room temperature can be used. In exceptional cases, other, but completely degassed water can be used.
- Determination of accuracy: For variable pipettes, the maximum volume, 50 % and 10 % of the maximum volume should be checked.
  100–1000 µL pipette volume < 2 %
  200 µL pipette volume < 1 %
- Determination of leakage-tightness: With a plastic hose approximately 20 cm in length pushed onto the pipette, draw in the amount of liquid and mark the meniscus. The fluid level must not change within 1 minute.
- Possible causes of pipetting errors: Contamination, residues inside the pipette, loose or false tips, damage to the cone to which the tips are attached, swollen seals, leaks, porous sealing rings and / or mechanical damage from overwinding or violence.

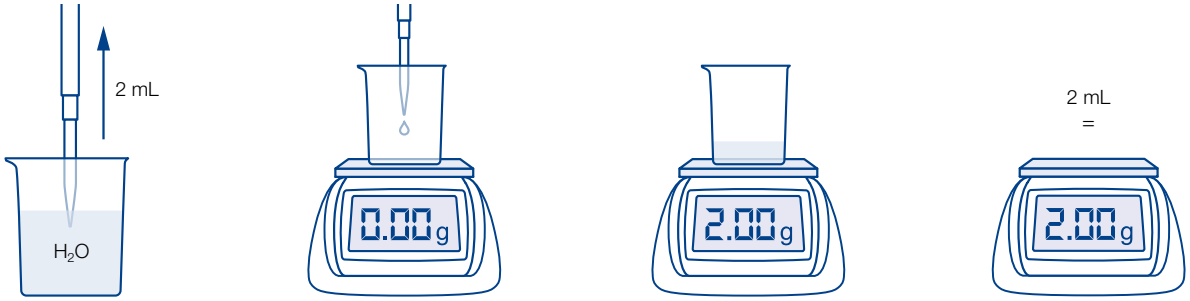


Figure 47: Calibration of Pipettes

5.4 How to deal with wrong results

If it seems likely that the measured value is incorrect, there are several possibilities to check the reading. The following points should be considered:

Implementation

- How was the test performed?
- Were the test instructions followed exactly?
- Were the correct volumes used?
- Were the response times observed?
- Was the proper reaction temperature maintained?
- Was the sample brought to room temperature?

Devices

- What kind of photometer / heating block do you use?
- When did you last calibrate your spectrophotometer? (Calibrate photometer if required!)
- Which sub-method have you selected?
- Are your pipettes checked and functioning?
- Does your heating block reach the required temperature? (10 °C increase in temperature doubles the reaction rate!)

IQC

- Have you performed a duplicate measurement? Are the values comparable?
- Have you performed a dilution / spiking? Have you obtained the expected values? (Ensuring that no matrix effects occur)
- Have you checked the test with a standard? What standard have you used, and what are the results?
- Did you compare the result with other measurement methods? (Authority, external laboratory, other photometer, etc.)

Sample

· What type of sample do you analyze?
· Does the sample look normal?
· What is the appearance of the sample? (Colored sample? Turbid sample?)
· What are the pH and temperature of the sample?
· How was the sample prepared for measurement? (Filtered, homogenized, preserved, etc.)
· May interfering ions be present in the sample?
· What measurement result can you expect?
· Why do you expect this measurement result? (From experience, appearance of the sample, etc.)

Test

· Which test is affected?
· Which lot number is used?
· How long can the test be stored?
· Do the test tubes or chemicals look different than usually?

6. Legal foundations

Preventive protection of waters as part of the ecosystem and ensuring public water supply and wastewater disposal are central tasks of environmental policies at the federal, state and municipal levels in Germany.

In the years of reconstruction after World War II, water protection could not keep up with the expansion of industrial development. So, by the late 1960s and early 1970s, water pollution had reached an alarming extent.

Therefore, the federal and state governments made water conservation a priority of their work. Through a variety of measures, water quality could be improved rapidly and sustainably. In particular, the industrial sources of water pollution were forced to adopt extensive water protection measures.

The high investments have indeed brought significant improvements. Until now, water protection remains an ongoing task. The general conditions of Germany, namely its geographical location in the centre of Europe, its high population density and degree of industrialization, continue to require special efforts in water conservation.

The Federal Government has set the stage for significant reduction of the discharge of hazardous substances and nutrients into water bodies through strict requirements for municipal and industrial wastewater treatment plants in the wastewater fee legislation. The polluters concerned must continue to make great efforts in the next years in order to achieve the objectives of the EU Water Framework Directive (WFD) and the EU Marine Strategy Framework Directive (MSFD). This applies in particular to reduction of the substantial nutrient inputs from agriculture and the improvement of surface water and groundwater.

6.1 European level

The Water Framework Directive (WFD) is important at the European level. This directive provides the legal framework for water policies in the EU. Its purpose is to align policies more strongly with a sustainable and an environmentally friendly use of water. In Germany, the EU Water Framework Directive was transposed into national law in the form of the German Water Resources Act (Wasserhaushaltsgesetz, WHG). The WHG is the central law of German water legislation.

6.1.1 EC guideline 2000/60/EC

The beginning of active European environmental policy dates back to 1973. Since that time, a number of individual directives for water protection have been adopted. After individual issues in the water sector repeatedly emerged in the European Union, the need was recognized to develop a comprehensive framework directive. This new directive should bundle all specific directives into a coherent overall concept.

In the early 1990s, the European Commission developed the idea of an ecologically oriented water protection policy intended to achieve improvement of ecological water quality and sustainable water utilization. Until 1999, the Framework Directive was revised and expanded several times, until the European Water Framework Directive (2000/60/EC WFD) finally entered into force on December 22nd, 2000.

The Water Framework Directive has the following main objectives:

- Rivers, lakes, groundwater and coastal waters shall be in a “good” ecological and chemical status by 2015.
- The management of surface waters is based on defined river basins.
- From 2010, the water supply must cover its own costs and may not be subsidized.

To achieve the main objectives, the WFD prescribes an ambitious timetable for the Member States:

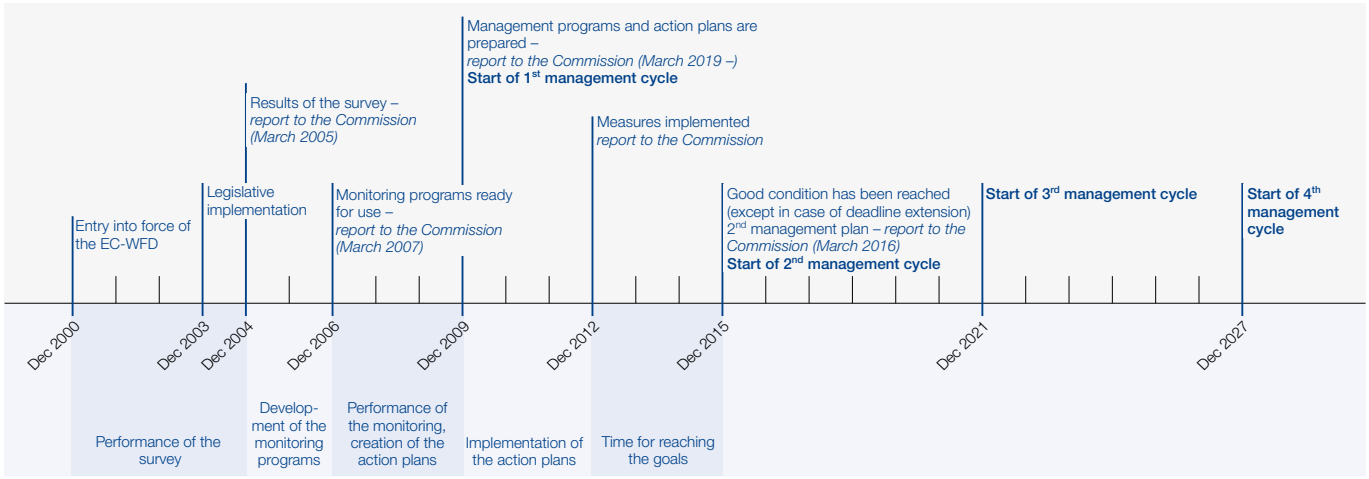


Figure 48: Schedule of the EC Water Framework Directive

6.1.2 Other relevant european directives

There are many other important European directives in the field of water and wastewater analysis in addition to the EC Water Framework Directive. The most important ones are listed below:

6.1.2.1 EC Municipal Waste Water Directive (91/271/EEC)

This directive governs the collection, treatment and discharge of municipal and industrial wastewaters to protect the environment from the effects of the effluent. This directive is intended to ensure treatment of these wastewaters at the Community level.

This directive entered into force on June 19th, 1991. By Directive 98/15/EC, specifically the discharges of municipal wastewater treatment plants have been defined more precisely.

6.1.2.2 Industrial Emissions Directive IED (2010/75/EU)

This EU Directive regulates the complete process in industrial enterprises from authorization to decommissioning. It consolidates seven previous guidelines relating to industrial emissions (including the IPPC Directive 2008/1/EC).

The Directive aims to prevent pollution from industrial plants or to reduce it as far as possible. To achieve this, industrial plants must use the best available technology (BREF documents).

6.1.2.3 Marine Strategy Framework Directive, MSFD (2008/56/EC)

As part of the implementation of the 6th EAP, on June 24th, 2005, the European Commission had presented a thematic strategy for protection and preservation of the marine environment and a proposal for a directive establishing a framework for community action in the field of marine environment.

This directive aims at achieving a good environmental status of the European marine waters (Baltic, North East Atlantic, Mediterranean, Black Sea) by 2020.

The MSFD entered into force on July 15th, 2008.

For implementation of this policy, there is a detailed schedule:

Timetable	Implementation
by 2010	Transposition into national law
October 2011	Start of public participation for the first reports
July 2012	· Delivery of the first reports to the European Commission · Initial assessment of the current environmental state of the seas · Determination of good environmental status, definition of environmental targets
by 2013	Publication of information on protected areas
by July 2014	Creation and performance of monitoring programs
by 2015	Creation of an action program designed to achieve or maintain good environmental status
by 2016	Practical implementation of the action program
by 2018	Progress reports on the programs to the European Commission
by 2020	Achieving good environmental status of the marine environment

Table 18: Implementation of the Marine Strategy Framework Directive

6.1.2.4 Directive on the Quality of Water Intended for Human Consumption (98/83/EC)

The European Union (EU) defines basic water quality standards for human use.

The aim of the Directive is to protect human health from the adverse effects of contaminated water, by ensuring consumability and purity of water. This directive entered into force on December 25th, 1998.

This directive defines minimum standards for drinking water in terms of microbiological parameters, chemical parameters and radioactivity.

6.2 Globally Harmonized System of Classification and Labeling of Chemicals (GHS)

GHS stands for “Globally Harmonized System of Classification and Labeling of Chemicals”, a globally uniform system of the United Nations for classification and labeling of chemicals.

GHS = Globally Harmonised System of Classification and Labelling of Chemicals.

All chemicals and mixtures of chemicals are, prior to preparation and sending, subject to classification and labeling requirements. All hazardous material properties must be rated and marked by danger symbols, so that people and environment are protected from adverse effects during the handling of substances.

Globally, there used to be diverse systems for the classification and labeling of chemicals. The result was that one substance or mixture might be classified and treated as dangerous in one country but not in another. This led to problems in transportation and commerce, among consumers and with regard to industrial safety. The aim of the new GHS is to globally unify the various systems and thus make the level of protection for human health and environment more transparent and comparable.

All chemicals and mixtures of chemicals are, prior to preparation and sending, subject to classification and labelling requirements.

The GHS Regulation globally regulates the harmonized classification and labeling for the marketing and handling of hazardous materials in the workplace. It also regulates the transport of dangerous goods, and the creation of safety data sheets.

6.2.1 Origin and development

During the World Summit on Sustainability 1992 in Rio de Janeiro, the participating countries requested for the first time that a harmonization of the classification and labeling of chemicals should be introduced worldwide.

“A globally harmonized hazard classification and compatible labeling system, including material safety data sheets and easily understandable symbols, should be available, if feasible, by the year 2000” (UNCED Agenda 21, chapter 19).

In 2003, the contents of GHS were first presented with the so-called “purple book”. It has since been continuously expanded and improved, with an updated version being published on average about every two years. Since 2008, the new classification and labeling system has been globally applicable.

The implementation of the GHS Regulation in European chemicals policies was specified by the new regulation (EC) no. 1272/2008. This new regulation, also known as CLP (Classification, Labeling and Packaging) Regulation, entered into force on January 20th, 2009.

The CLP Regulation defines, for example, the criteria by which a substance or mixture is to be classified, but also how substances or mixtures rated as hazardous are to be packaged and marked.

It gradually replaces the hitherto valid Substances Directive (67/548/EEC) and the Dangerous Preparations Directive (1999/45/EC). By June 01st, 2015, these two directives will be repealed. Long grace periods are provided for the transition to the new regulation. Thus, the GHS Regulation has been mandatory for substances since December 01st, 2010, for mixtures from June 01st, 2015.

Label	Old labeling	New labeling
Substances	Prohibited in the meantime	Allowed since Jan 20, 2009, mandatory since Dec 01, 2010
Mixtures	Allowed up to Jun 01, 2015 (stocks: + 2 years)	Allowed since Jan 20, 2009, mandatory since Jun 01, 2015
Safety data sheet	**Old classification**	**New classification**
Substances	Mandatory until Jun 01, 2015	Allowed since Jan 20, 2009, mandatory since Dec 01, 2010
Mixtures	Mandatory until Jun 01, 2015	Allowed since Jan 20, 2009, mandatory since Jun 01, 2015

Table 19: Transition phases according to the CLP Regulation

By the end of the transition periods, labeling according to the old directive as well as to the new GHS is possible. Double labeling, however, is prohibited and not allowed.

6.2.2 Hazard classes: assignment of hazardous properties

In contrast to the old Substances Directive and in accordance with GHS, hazardous properties are rated using 28 hazard classes. Previously, 15 so-called risk characteristics were used for rating. By extension to 28 risk classes, a much more nuanced distinction of hazards is possible. The risk classes comprise physico-chemical hazards, hazards to human health and hazards to the environment.

Hazards	Substances directive hazard characteristics	GHS hazard class
Physico-chemical	5	16
Health	9	10
Environment	1	2

Table 20: Comparison of risk characteristics according to DSD and hazard classifications according to GHS

An important aspect is that the severity of the hazard is no longer directly linked to the hazardous characteristic. Instead, the hazard classes are subdivided into up to four categories or sub-classes or seven types. The risk decreases with increasing numbering or with consecutive letters.

The highest risk is therefore in category 1. The old hazardous characteristics “very toxic”, “toxic” and “harmful” are all implemented in the class “Acute toxicity” according to GHS. A distinction is made by the individual subcategories. The same applies to the previous risk characteristics “extremely flammable”, “highly flammable” and “flammable”. In the future, differences are made also by aggregate state and hazard intensity according to the subcategories.

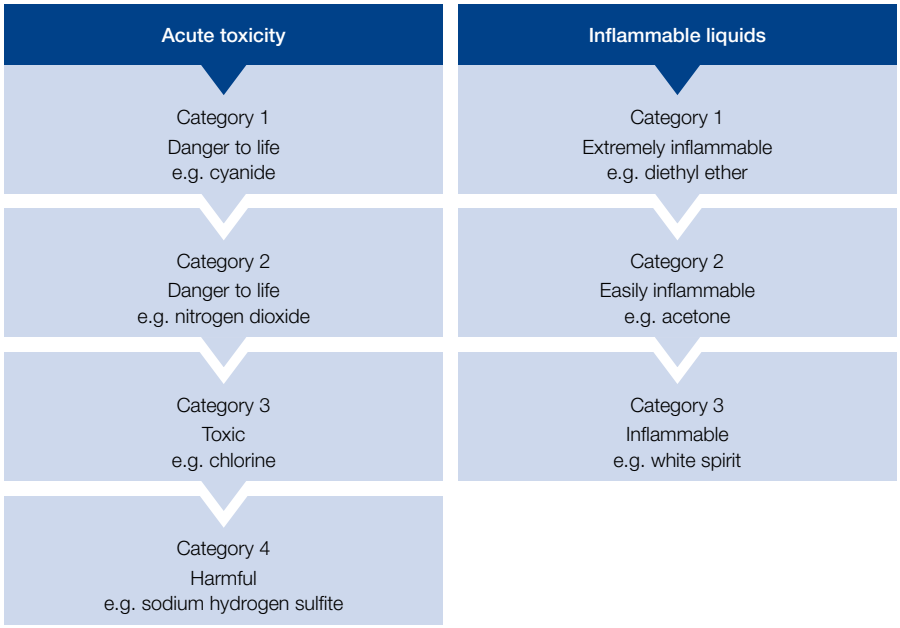


Figure 49: Context of numbering and risk

The names of the individual hazard classes according to GHS and their classification as physical-chemical, health-related or environmental hazards are listed in the following table.

Abbreviation	Type of risk	German designation
Expl.	Physical risk	Explosive substances / mixtures and articles containing explosives
Flam. Gas	Physical risk	Flammable gases
Flam. Aerosol	Physical risk	Flammable aerosols
Ox. Gas	Physical risk	Oxidizing gases
Press. Gas	Physical risk	Gases under pressure
Flam. Liq.	Physical risk	Flammable liquids
Flam. Sol.	Physical risk	Flammable solids
Self-react.	Physical risk	Self-reactive substances and mixtures
Pyr. Liq.	Physical risk	Pyrophoric liquids
Pyr. Sol.	Physical risk	Pyrophoric solids
Self-heat.	Physical risk	Self-heating substances and mixtures
Water-react.	Physical risk	Substances and mixtures which release flammable gases upon contact with water
Ox. Liq.	Physical risk	Oxidizing liquids
Ox. Sol.	Physical risk	Oxidizing solids
Org. Perox.	Physical risk	Organic peroxides
Met. Corr.	Physical risk	Corrosive to metals
Acute Tox.	Health risk	Acute toxicity
Skin Corr. Skin Irrit.	Health risk	Corrosion / irritation to the skin
Eye Dam. Eye Irrit.	Health risk	Serious eye damage / eye irritation
Resp. Sens. Skin Sens.	Health risk	Sensitization of the respiratory tract or skin
Muta.	Health risk	Germ cell mutagenicity
Carc.	Health risk	Carcinogenicity

Abbreviation	Type of risk	German designation
Repr.	Health risk	Reproductive toxicity
STOT SE	Health risk	Specific target organ toxicity (single exposure)
STOT RE	Health risk	Specific target organ toxicity (repeated exposure)
Asp. Tox.	Health risk	Risk upon aspiration
Aquatic Acute Aquatic Chronic	Environmental risk	Hazards to the aquatic environment
Ozone	Environmental risk	Damages the ozone layer, additional EU hazard class

Table 21: Hazard classes according to GHS

6.2.3 Signal words

The signal words are a new marking element according to the GHS Regulation. According to the GHS Regulation, there are two signal words:

· DANGER (for serious risk categories)

· WARNING (for less serious risk categories)

Signal words inform about the relative hazard level. Persons handling this substance or mixture are to be made aware of the danger. The signal word “DANGER” describes the serious dangers and replaces the “WARNING” when both hazard classes or differentiations are present. The signal word “WARNING” is reserved for the hazard categories with lower risk.

6.2.4 GHS icons

The GHS Regulation dictates nine icons for hazardous substances. These icons consist of black symbols in red squares and replace the old hazard symbols with their hazard descriptions.

Icon	Designation	Coding	Signal word
	Exploding bomb	GHS01	DANGER / WARNING
	Flame	GHS02	DANGER / WARNING
	Flame over circle	GHS03	DANGER / WARNING
	Gas cylinder	GHS04	WARNING
	Corrosive effect	GHS05	DANGER / WARNING
	Skull and crossbones	GHS06	DANGER
	Exclamation mark	GHS07	WARNING

Icon	Designation	Coding	Signal word
	Health hazard	GHS08	DANGER / WARNING
	Environment	GHS09	WARNING

Table 22: Icons according to GHS

6.2.5 Hazard phrases according to GHS

The hazard phrases are not comparable to the previous R-phrases from the material and preparation directive. These standardized text modules describe the nature and severity of the hazard. They are listed on the label. Inner packaging and packaging for products with bottles of no more than 125 mL and lesser risks do not require hazard phrase.

H301		
H	3	01
Indicates Hazard Phrase	Grouping: 2 = physical dangers 3 = dangers to health 4 = dangers to the environment	Serial number

Figure 50: Structure of hazard phrases

Some R-phrases and other labeling elements which are not covered by the GHS system of the UN were transposed into European H phrases (EUH phrases) to maintain the EU protection level. They do not lead to classification into any hazard class and are therefore not listed in section 2 of the safety data sheet.

6.2.6 Precautionary notes (P phrases) according to GHS

The recommended measures to limit or prevent harmful effects of chemicals during use are formulated based on these precautionary phrases. These standardized contents are similar to the S-phrases from the Substance and Preparation Directive. The criteria for the precautionary phrases are defined in Annex IV, Part 1 of the GHS Regulation. For example, a maximum of six precautionary phrases shall be used, unless the degree of hazard requires a higher number. Again, the small amount rule applies.

P102		
P	1	02
Indicates Precautionary Phrase	Grouping: 1 = general 2 = precautionary measures 3 = recommendations 4 = storage information 5 = disposal	Serial number

Figure 51: Elements of P phrases

6.2.7 Labeling system

The labeling shall inform persons who handle a substance or a mixture about the associated risks. The selection of the labeling elements depends primarily on the classification results.

Each risk category comprises an icon, a signal word, an H phrase and several P phrases.

However, a substance or a mixture of substances can have several hazardous properties. This means that to a substance or mixture several hazard classes and hazard categories can be assigned, which is to be evidenced by several icons, signal words, H and P phrases.

Each icon is listed only once. For the signal words, only the one with the highest priority is used. The H phrases are always indicated, as these characterize the respective hazard category. In most cases, a large number of P statements is to be listed. Therefore, the number is to be reduced to a maximum of six P phrases per substance or mixture. The P phrases must be selected by the manufacturer or sender themselves. Since they are not legally defined, the safety data sheets of the individual companies may vary on this point.

REACh = Registration, Evaluation, Authorisation of chemicals

6.3 Registration, Evaluation, Authorization of Chemicals (REACh)

REACh (Regulation (EC) 1907/2006) is an EU chemicals regulation, which entered into force on June 01st, 2007. REACh is the abbreviation for “Registration, Evaluation and Authorization of Chemicals”.

The REACh Regulation is to ensure a high level of protection for people and environment in the handling of chemicals. At the same time, REACh ensures free movement of chemicals in the internal market and thus promotes competitiveness and innovation.

Manufacturers, importers and users must take own responsibility for chemicals under REACh. They must ensure that the chemicals manufactured and marketed are used safely (principle of direct responsibility).

The REACh Regulation is considered one of the strictest chemicals laws in the world and, as an EU regulation, it is in force in all member states.

6.3.1 Why REACh?

REACh is based on old chemicals legislations and harmonizes and simplifies the previously existing chemicals legislation.

Introduction of REACh is intended to overcome the weaknesses of previously existing chemicals legislations. So far, authorities used to rate the safety of chemicals. A particular weakness of the old system was that no systematically collected information was available about the hazards to persons and the environment for chemicals placed on the market before 1981 (“legacy” substances). Legacy substances were to be tested only gradually, or whenever a substance rating of the authorities had gaps or a safety hazard was to be assumed.

The registration of new substances, by contrast, entailed a complex application procedure, so that often inadequately tested legacy substances were resorted to. Overall, the existing process was slow and thus impractical.

REACh creates a uniform system: With the introduction of chemicals into the market, manufacturers and importers are obliged to register them and assess the risks independently. Registration is required if at least one ton per year of the chemical is produced or imported.

The tasks of the authorities are now in the provision of assistance with the registration, in the examination of registrations and in the regulation of substances which are of very high concern or which have particular hazards for humans and the environment.

6.3.2 Implementation of REACh

The Implementation of REACh takes place in three steps.
· Registration
· Evaluation
· Approval

6.3.2.1 Registration

The main challenge for manufacturers and importers is the evaluation of the chemicals and their registration with the ECHA (European Chemicals Agency). The registration is carried out in three phases: The first phase ended in November 2010, the second in November 2013, and the third phase must be completed by mid-2018.

Timetable	Implementation
01 June 2007	Entry into force of REACh
01 June 2008	Beginning of pre-registration
01 December 2008	End of pre-registration
01 January 2009	Publication of the pre-registered substances
01 June 2009	ECHA proposes substances for Annex XIV
01 December 2010	End of registration for · substances ≥ 1,000 t/y · CMR substances ≥ 1 t/y · Environmentally Hazardous Substances ≥ 100 t/a
01 December 2011	First schedule for the assessment is completed
01 June 2013	Registration deadline for substances ≥ 100 t/a
01 June 2018	Registration deadline for substances ≥ 1 t/a

Table 23: Implementation of the REACh Regulation

For registration, sufficient data must be submitted to allow assessment of the substance. For quantities of 10 tons or more per year, the manufacturer or importer must create a chemical safety report explaining hazards and exposure scenarios.

The amount of data to be submitted depends on the quantity of the chemical substance produced or imported. The registration of substances in mixtures is subject to separate regulations.

"No data, no market"

6.3.2.2 Evaluation

The registrations are evaluated by the authorities. The ECHA checks all registrations for completeness. In addition, selected chemicals are assessed for characteristics of very high concern and risks for humans and the environment.

Substances are considered of very high concern (SVHC) if they meet at least one of the following criteria:

· Carcinogenic, mutagenic or toxic for reproduction or

· Toxic, persistent in the environment and accumulating in organisms or

· Very persistent in the environment and very strongly accumulating in organisms or

· Having similar properties of concern (e.g. hormonal effect)

6.3.2.3 Approval

Approvals refer to substances considered of very high concern (SVHCs). REACh strives to replace such chemicals in the long run with materials of lesser concern, provided that the alternative substances are economically and technically qualified.

Under REACh, such dangerous substances are included into a "candidate list" from which the EU Commission in turn prioritizes substances required to be approved. Concerning possible substitution with a less hazardous alternative substance, a date is specified until which the substance may still be used in certain areas. In addition to approvals, restrictions may be issued that relate not only to SVHCs.

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Reliable COD Analysis

- No risk of leaking gases
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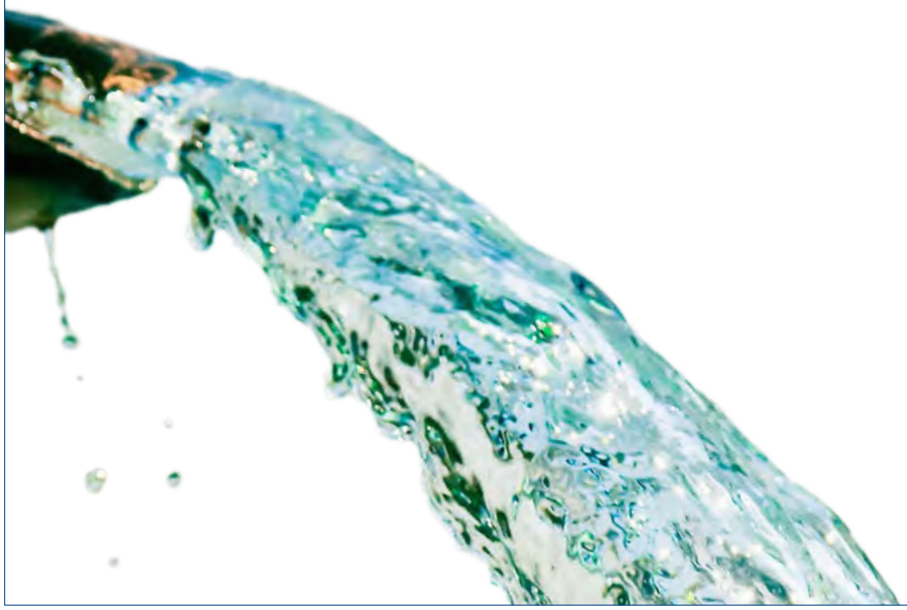
- Hg-free version available
- 12 measurement ranges available for all requirements and demands



7. Annex

7.1 Conversion tables and units

Base quantity	Symbol	Dimension symbol	Base unit	Unit symbol
Current strength	*I*	I	Ampere	A
Length	*l*	L	Meter	m
Luminous intensity	I_V	J	Candela	cd
Mass	*m*	M	Kilogram	kg
Quantity of substance	*n*	N	Mol	mol
Temperature	*T*	Θ	Kelvin	K
Time	*t*	T	Second	s

Table 24: SI based quantities and units

Quantity	Physical quantity	Symbol	Dimension	SI unit	Other possible units
Energy	Work Energy	*W, E*	$M L^2 T^{-2}$	J (Joule)	Nm (Newton meters) kWh (kilowatt hour) cal (calorie)
Surface	Area	*A, S*	L^2	m^2	A (are) ha (hectare)
Length	Length Diameter Width Height, Depth Wavelength	L d b h λ	L L	m m	mm cm Å (Angstrom) nm (Nanometer) Å (Angstrom)
Power	Power	P	$M L^2 T^{-3}$	W (watts)	PS
Quantity of substance	Quantity of substance	n	N	mol	eq
Mass	Weight	m	M	kg	g t (ton)
Molar mass	Molar mass	M	$M N^{-1}$	$g\ mol^{-1}$	
Temperature	Temperature difference	ΔT	Θ	K	°C °F
Volume	Volume	V	L^3	m^3	L (Liter)
Molar volume	Molar volume	V_m	$L^3 N^{-1}$	$m^3\ mol^{-1}$	
Time	Time, duration	*t*	T	s	min h (hour) d (day) a (year)

Table 25: Important quantities and units

Unit	Conversion
1 µg	1 × 10–6 g = 10–9 kg
1 mg	0.001 g
1 kg	1000 g
1 mL	0.001 L = 1000 µL
1 ppb	0.001 µg/mL
1000 ppb	1 µg
1 ppm	1 µg/mL = 1 mg/L
1000 ppm	1 g/L

Table 26: Frequently required conversions

7.2 Dictionary

Dictionary water analysis	
A	
AAS	Atomic absorption spectroscopy, analytical method
Absorbance	A dimensionless measure of extinction or attenuation of light in colorimetry and photometry.
Absorption	General: The taking up of a substance. In photometry: a colored solution in the cuvette absorbs light.
Accuracy	Sum of correctness and precision. Measure of the approximation of the reading to the "actual" value. Basically, the accuracy of measurement results depends on the precision of the measurement method. The number of decimal places of a digital display is not a measure of accuracy; it should be kept to a justifiable minimum.
Acid capacity	The acid capacity is defined as the amount of hydrochloric acid that can be added to a sample until a pH value of 4.3 is reached (often abbreviated as $KS_{4.3}$). The term is primarily used for waters low in buffering substances such as phosphate, ammonium and sulfide ions or calcareous particles. The term "acid capacity" is obsolescent, the new term to be used is: Alkalinity.
Acidity (base capacity up to pH 8.3)	Acidity or acid content of a solution. It increases with the abundance of H_3O^+ ions. Measure of the ability of a compound to release hydrogen ions. In water caused by mineral acids and free CO_2.
ACRON	Program for analysis and evaluation of historical data. Also often used in sewage treatment plants for convenient measurement reporting or preparation of monthly and annual reports to authorities. The measurement data are transmitted from *NANOCOLOR*® spectrophotometers to ACRON via PC software.
Activated carbon	Porous highly pure carbon having a large surface area (300–2000 m^2 per gram). Particularly suitable as an adsorbent. Used for gas cleaning (e.g. in respirators) or for clarification of liquids.
Activated sludge process	Biological wastewater treatment in which wastewater is mixed with activated sludge and aerated. The activated sludge is subsequently separated in the secondary clarifier from the purified waste water and fed into the aeration tank as return sludge
Adsorption, adsorb, adsorptive	Attachment of a substance to a surface by molecular forces, e.g. of activated carbon
Aerobic	Depending on the presence of dissolved oxygen. Often referring to the metabolism or life of organisms that require elemental oxygen. In wastewater technology e.g. the activated sludge process.
Alkalinity (acid capacity up to pH 4.3)	Measure of the buffering capacity of the water. Content of carbonates, bicarbonates, hydroxides, dissolved salts in a solution. Also a summary effect and material characteristic. If the residual acid capacity is too low, the pH drops into the acidic range.
Ammonification	Conversion of nitrogen compounds to ammonium by bacteria
Ammonium	Ionic nitrogen-hydrogen compound (NH_4^+) in which the nitrogen is present in the oxidation state -3. Ammonium is in equilibrium with fish-toxic ammonia (NH_3), which is formed upon pH shifting into the basic range.
Amount of substance	SI base quantity indicating the number of particles of a substance.
Anaerobic	Processes under exclusion of oxygen
Analysis	Systematic examination, wherein the chemical compound or the sample is decomposed into its constituents.
Analysis method	Full description of the application of a chemical reaction or a physical principle for determining characteristics of a substance or mixture
Analytical procedure	Implementation of an analysis method according to predefined and precisely described rules that an experienced user can perform. Parameters describing an analytical procedure are: Selectivity / specificity, linearity, robustness, recovery and reproducibility = requirements for validation.
Analytics	Analytical chemistry is a branch of applied chemistry. It deals with the determination of the type (qualitative analysis) and the amount (quantitative analysis) of a substance or mixture of substances. In general, it uses analytical methods comprising sampling, sample preparation, separation, identification and documentation.
Anions	Electrically negatively charged atoms or groups of atoms, e.g. Cl^-, ClO_2^-, CrO_4^{2-}, CN-, F-, NO_3^-, NO_2-
Anoxic	Processes without dissolved but with bound oxygen
AOX / EOX	Totality of the adsorbable or extractable organic halogen compounds, which are particularly important from an environmental and toxicological perspective.
Aqua regia	Aqua regia consists of 1 part of concentrated nitric acid and 3 parts of concentrated hydrochloric acid. Aqua regia dissolves even gold, the "king" of metals, and platinum. Aqua regia decomposition is used among other things for heavy metal and sludge analysis.
ATP	Abbreviation for adenosine triphosphate. Important as metabolic carriers of chemical energy. Used by enzymes which catalyze the synthesis of adenosine diphosphate and inorganic phosphate. ATP measurements are carried out using the MN luminometer.
B	
bar	Physical pressure unit (1 bar = 10^5 Pa)
Biological mineralization	Degradation of organic substances to water, minerals and carbon dioxide
Blank	Reference value for the zero position of a photometer. The blank value is test-dependent, e.g. a sample solution without reagents, sample solution with several reagents, distilled water with all reagents, or a "synthetic" zero solution enclosed with the test. In the new *NANOCOLOR*® photometers, most zero values are already pre-programmed.

Dictionary water analysis	
BOD_5	Biochemical or biological oxygen demand, cumulative parameter (action parameter). The amount of oxygen in mg per liter of water that is consumed by the micro-organisms within 5 days at 20 °C to decompose the contained organic contents / contaminations by oxidation. The BOD_5 permits a statement about the organic contamination of the water or the biochemically useful degradation behavior. For domestic sewage, about 300 mg/L O_2 are typical, while pure river waters have a BOD_5 of about 1–3 mg/L O_2.
Buffer	Chemical agents that provide a certain degree of pH stability. Typical buffering agents are acetates, phosphates and citrates.
Buffering capacity	The buffering capacity indicates the stability of the pH of a solution upon addition of strong bases or strong acids.
C	
Calibration	Determination of the analysis function involving the respective instrument and the sample matrix for the specified method. The calibration is valid only for the scope of the method described. Also used for the validation of measuring instruments in case there are no legal requirements, e.g. for quality assurance in accordance with DIN EN ISO 9001. Calibration requires the availability of a higher-order standard. Detection of a deviation from a known correct standard with logging.
Carbonate hardness	Part of the total hardness equivalent to the bicarbonate and carbonate contained in the water.
Carcinogenic substances	Cancerogenes
Cations	Positively charged atoms or groups of atoms, e.g. K^+, Cu^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}
CE marking	An EU label as “passport for industrial products” or labeling of industrial products for the free movement of goods within the European Economic Area (EEA). “CE” was, inter alia, derived from the French Communauté Européenne or Spanish Comunidad Europea. The marking is not a safety or quality label in the strict sense. The marking is directed not to consumers, but rather to the authorities, thus being administrative in character.
Cuvette tests	Cuvettes in which the required reagents are often already pre-measured, allowing very swift evaluation. Extremely easy to use.
CFC	Chlorofluorocarbons are chemically very stable and non-flammable. They destroy the ozone layer in the stratosphere, where they accumulate because of their durability.
CHC	Abbreviation for chlorinated hydrocarbons. Organic compounds in which one or more hydrogen atoms are replaced by chlorine atoms (e.g. in solvents, pesticides, plastics, etc.).
Classification limit	Threshold concentration above which a substance or preparation is to be classified as hazardous.
GHS	Globally Harmonized System of Classification and Labeling of Chemicals
COD	Chemical oxygen demand, cumulative parameter (action parameter). Key parameter for the statutory wastewater charge. Chemical oxygen demand is a measure of the pollution and oxidizability of mostly organic contents / contaminations by potassium dichromate / sulfuric acid.
Coefficient of variation of a procedure	According to DIN 38402 (A 51 – Calibration of analytical methods), the coefficient of variation VXO is a relative procedural standard deviation from the work average. It characterizes the achievable accuracy of an analytical test. Very well-functioning tests have a process variation coefficient of about 1 %.
Colloids	Finely distributed particles (solid particles or droplets) in a dispersion medium (solid, gas or liquid). The individual particles have sizes in the nanometer to micrometer range.
Colorimetry	Analytic method making use of visual comparison under natural light conditions. General: Determination of the concentration of colored substances in solution by comparative light absorption measurement
Comparative measurement	Comparative examination of a sample by other users or other analytical methods
Comparator	Test vessel for visual assessment of color development. By comparison with a standard color scale, a measurement value can be assigned.
Complexing agents	Reagents which form stable compounds with most heavy metals, e.g. EDTA, NTA and others
Concentration	Mass concentration (mass per volume), e.g. mg/L or g/L, is indicated with “β”. Molar concentration (molarity), e.g. mol/L or mmol/L, is by contrast indicated with “c”. Although “β” is the correct symbol for mass concentration, for simplicity often c is used as the symbol.
Conductivity, electrical	Property of a substance to permit flow of electric charge carriers (free or bound electrons, positive or negative ions). It is a measure for the quantity of ions contained in the water. The higher the number of ions, the higher the conductivity. A Conductivity measurement provides information about the salt load of a water. The unit is Siemens/meter [S/m].
Confidence interval	Is specified in the use of standard solutions. Despite differences in mode of operation, temperature, slight deviation in the calibration of laboratory equipment and other influences, the concentration measured must be within the confidence interval (tolerable measurement range).
Contamination	Soiling with radioactive, chemical or microbially active substances
Correction value	In photometry, intrinsic color and turbidity can cause higher absorbance and thus distortion of the measured value. This deviation is compensated by the correction value. The correction values are parameter-dependent. For more information, please see the photometer manuals.
Correctness	Deviation between the analysis and the “actual” value. The difference from the “actual” value of an analysis should be as low as possible.
Cumulative parameters	Summary action and material characteristic, e.g. COD as the sum of all oxidizable (oxygen-consuming) contents in the water, BOD_5, TOC, AOX, etc.

Dictionary water analysis	
D	
Decomposition, chem.	Chemical process for converting insoluble or complexed materials into an ionogenic form accessible to analysis
Degradability	The degree of biologically or chemically induced decomposition of organic compounds, mainly based on metabolic processes of micro-organisms.
Denitrification	Nitrogen removal in wastewater treatment plants. Biodegradation of nitrate via nitrite to gaseous nitrogen. The requirements for denitrification are a lack of oxygen and easily degradable organic compounds. Denitrification takes place in soil.
Detergents, surfactants	Detergents / surfactants consist of a hydrophilic and a hydrophobic part and thus are surface-active agents. They significantly accelerate purification processes, alone or in combination with other compounds. Nowadays, they must be degradable in waste water treatment plants. Three types are differentiated: anionic, cationic and non-ionic surfactants.
DEV	Abbreviation for “Deutsches Einheitsverfahren zur Wasser-, Abwasser- und Klärschlammuntersuchung” (German standard method for examination of water, waste water and sludge). Published by the Specialist Group for Water Chemistry in the German Chemical Society and the Committee for Standardization in Water Management.
DIN	Abbreviation for “Deutsches Institut für Normung” the German institut for norms
Dioxins	Dioxin is a frequently used, though imprecise collective term for 75 related substances. More precisely, they are called dibenzo paradioxines. They all share a basic structure of carbon, hydrogen and oxygen atoms. Chlorinated dibenzodioxins are used in plastics, detergents, disinfectants, plant protection products, paints and varnishes. Dioxins are toxic.
Direct dischargers	In general, these are larger industrial companies, which have their own wastewater treatment plants and may discharge wastewaters, with the approval of the water authority, directly into a receiving water. Water treatment plants likewise discharge directly.
DOC	DOC, Dissolved Organic Carbon = dissolved organic carbon in the filtrate (membrane filter with a pore size of 0.45 µm) of a sample. See also TOC. The dissolved fraction of TOC corresponds to the DOC.
DS	Abbreviation for dry sludge residue in sludge analysis. The values are given in mg/kg dry weight.
E	
EBC	European Brewery Convention
EDTA	Abbreviation of ethylenediaminetetraacetic acid, a commonly used complexing agent.
Emission Principle	Introduced with the 4th Amendment to the German Water Resources Act in 1976. It assumes that from comparable wastewater discharges into a body of water comparable discharge requirements can be derived.
Emulsion	Dispersed (finely distributed) material of at least two not or only partially miscible liquids. Distribution in the form of minute drops.
Environmental analysis	Totality of all analytical methods for the objective determination of pollution of all kinds
Enzymes	Proteins that are involved as catalysts in almost all chemical reactions in the body.
EPA	Abbreviation for “Environmental Protection Agency”: agency of the federal government of the United States of America, with the purpose of protecting human health and environment.
Eutrophication	Over-fertilization, abundance of nutrients due to organic substances. It can lead to a so-called “collapse” of a body of water. The result is formation of digested sludge with distinctively smelling degradation products such as hydrogen sulfide, ammonia as well as the odorless gas methane. Enrichment of water with nutrients, especially nitrogen and / or phosphorus compounds, leads to accelerated growth of algae and higher forms of plant life. (From: Council Directive on Municipal Waste Water Treatment)
Extraction	Method for isolating a substance. For this purpose, e.g. an organic solvent may be used for the extraction of (non-polar, organic) substances from water. The extraction method is used: · for water-insoluble colored complexes · to increase the color intensity of the color complex · to increase the selectivity of the desired substance · to concentrate the color complex
F	
FAU	FAU, Formazine Attenuation Unit
Flocculation	Aggregation of finely grained to colloidal particles suspended in aqueous systems to form coarser flakes. Flocculation can be achieved by flocculants. The objective of flocculation is an easier separation of the solids.
FNU	FNU, Formazine Nephelometric Unit = turbidity unit determined by measuring the intensity of the scattered radiation at an angle of 90° from the incident light path when using an aqueous formazine solution for calibration. Denoted in accordance with DIN EN 27027 (03/94) as Formazine Nephelometry Unit. The turbidity of a specified stock solution is 400 FNU.
G	
German Chemicals Prohibition Ordinance (Chemikalien-Verbotsverordnung, ChemVerbotsV)	German federal law defining bans and restrictions on the marketing of dangerous substances, preparations and products under the German Chemicals Act. The law establishes specifications for demonstrations of competence.
German hardness degrees	1 °d = 1.253 °e= 17.8 mg/L $CaCO_3$ = 10 mg/L CaO = 7.15 mg/L Ca = 0.18 mmol/L $CaCO_3$
German Sludge Ordinance	Legal basis from April 15th, 1992, regulating the use of sewage sludge on agricultural, forestry or horticultural soils.

Dictionary water analysis	
German Wastewater Charges Act (Abwasserabgabengesetz, AbwAG)	German Federal Law of September 13th, 1976, most recently amended in September 2014, according to which upon discharge of wastewater into a water body a fee depending on quantity and contamination is charged by the authorities.
German Water Resources Act (Wasserhaushaltsgesetz, WHG)	Fundamental federal environment / water protection legislation. This law is the basis for water laws of the individual states, which are in turn pivotal for further legislation.
Guide value	In accordance with § 4 of the German Wastewater Charges Act (Abwasserabgabengesetzes, AbwAG), the guide value is the value that must be met on average. If the guide value is greater than or equal to half the maximum value, it is used as a reference value.
H	
H phrase	H phrases identify hazards.
Homogenization	Preparation of a uniform (homogeneous) mixture. Requirement for the determination of real and comparable results. DIN 38402 defines e.g. homogenization of heterogeneous waters.
Humic substances (HS)	Multi-component mixtures, in which neither the number of mixture partners nor their exact structures are known. For detection, cumulative parameters such as DOC or UV absorbance must be used. Humic substances have polar properties and a macromolecular structure. Sometimes they account for the yellow-brown coloring of water. Most of the organic substances that occur in soils, sediments, waters and seas, are classified as humic substances. Humic substances interact with almost all organic and inorganic substances.
Hydrophilic	Attracting water (Greek hydro = water, philos = loving)
Hydrophobic	Repelling water (Greek hydro = water, phobas = fear)
Hydroxides	All hydroxides consist of the hydroxide ion (OH^-) as a negative component and a positive counterpart (e.g. Na^+). Soluble hydroxides show a strong alkaline reaction in water.
I	
Indirect dischargers	In general, smaller industrial companies. They discharge their wastewater first into the local sewer system and then via a water treatment plant into the receiving water. Indirect dischargers are subject to municipal sewer utilization regulations, which in turn may determine guide, limit or monitor values for emission control.
Initial treatment	Physical and / or chemical treatment of municipal waste water by a process involving sedimentation of suspended solids, or other processes in which – based on the values in the feed – the BOD_5 is reduced at least by 20 % and the total suspended solids by at least 50 %. (From: Council Directive on Municipal Waste Water Treatment)
Internal quality control (IQC)	Quality assurance measures which the user of an operating method performs independently.
ISO	International Organization for Standardization: international standard-setting body
K	
Kjeldahl Nitrogen (Total)	Sum of organic nitrogen and ammonia nitrogen
L	
LC (LC_{50})	Lethal (fatal) concentration at which 50 % of the test animals died. Notation of acute toxicity tests (e.g. LC_{50} inhal.)
LD (LD_{50})	Lethal (fatal) dose, e.g. in the case of one-time ingestion through the mouth (pharynx), at which 50 % of the test animals died. Notation for acute toxicity tests results (e.g. B. LD_{50} orally)
Leachate	Generally rainwater that seeps through the permeable soil layers. In landfills, the water accumulating on the base seal is called leachate. It is caused by rainfall and drainage of residual waste deposited.
Limit of detection	The minimum content of an analyte from which measured value conclusions concerning the presence of the analyte can be drawn with sufficient statistical probability.
Limit of quantification	The minimum content of an analyte from whose measured value conclusions as to the presence of the analyte can be drawn with high statistical probability. The quantification limit corresponds to the lower limit of the measurement range.
Load	Absolute amount of a pollutant within a specified unit of time.
Long-term stability	Technical specification for photometers. It includes a possible device-related and system-related deviation in display accuracy during continuous operation. The value is mostly given in E/h (absorbance per hour). Today, typical values are < 0.003 E/h.
Lyophilisation	Freeze-drying of reagents. Lyophilisates have excellent dissolution properties.
M	
MAK	Maximum airborne concentration of a substance at the workplace at which the health of the workers is generally not compromised.
Masking agents	Reagents that can be used in a test-specific manner for binding (masking) interfering substances. Masked substances can be unmasked again. Example: Masking of Zn^{2+} by CN^- as $Zn(CN)_4^{2-}$; release by chloral hydrate
Mass	Basic physical parameter, indicated in the unit kilogram.
Matrix interferences	Sum of all the contents that affect the chemical reaction and thus the measuring result positively or negatively.
Maximum value	According to § 4 of the German Wastewater Charges Act (Abwasserabgabengesetz, AbwAG), the value that must not be exceeded in any case. See also guide value, reference value.

Dictionary water analysis	
MBAS	Methylene blue active substances. DIN 38409 requires this measurement for anionic surfactants.
Measurement range	Indicated range of an analytical method in which a predetermined deviation in the concentration stated is not exceeded. Possible measures in case the range is exceeded are the selection of another cuvette, dilution, enrichment of the contents of interest or selection of another test.
Mineralization	Decomposition of organic matter, mainly by micro-organisms, to inorganic substances. In chemistry, the term is also used for the conversion of organic to inorganic compounds.
mol	Unit of the amount of substance n
Molar mass	Quotient of the mass m and the amount n of a substance: The SI unit is kg/mol; in chemistry g/mol is usual. The molar mass of a compound can be calculated if the sum formula is known.
Municipal wastewater	Domestic waste water or mixture of domestic and industrial wastewaters. (From: Council Directive on Municipal Waste Water Treatment)
N	
NANOCOLOR®	Name of the photometric analysis system by MACHEREY-NAGEL
NANOCOLOR® *NanOx*	Solid reagent for performing decompositions in a heating block or in a microwave oven
NANOCONTROL	Quality assurance product by MACHEREY-NAGEL, e.g. standard solutions
NANOFIX	Freeze-dried reagent in plastic capsules. *NANOFIX* has excellent dissolution properties and can be dosed with highest accuracy.
Nephelometry	Optical measurement of turbidity caused by suspended solids in liquids and gases, also referred to as turbidimetry.
Nitrification	Nitrogen oxidation. Biodegradation of ammonium to nitrite and then to nitrate under copious supply of oxygen in wastewater treatment plants. Conversion runs from NH_4^+ to NO_2^- (nitrite ion) and thence to NO_3^- (nitrate ion) under the influence of the nitrifying bacterial genera Nitrosomonas and Nitrobacter.
Nitrogen parameters	Important compounds in drinking water and waste water that contain nitrogen; e.g. nitrate, nitrite, ammonium, organic nitrogen compounds
Non-bleeding	Designation of a property of indicator strips. In pH-Fix indicator strips, the indicator dyes are linked to the cellulose fiber so that the dyes do not “bleed” even in strongly alkaline solutions.
NTU	NTU = nephelometric turbidity unit, For measurements with units greater than 1000 NTU, inclusion of other scattered light detectors (measurement angles lesser and greater than 90°) is needed to obtain an accurate measurement result. Due to this revised measurement mode, the formazine unit as standard solution is referred to as NTU.
Nutrient contamination level	The oxygen consumption caused by nutrients (mainly phosphates and nitrates) in water bodies. Nutrients promote eutrophication. From a scientific perspective, phosphates burden water bodies 7 times as much as nitrates. Complements the rating system of oxygen demand levels; currently 5 levels are defined.
O	
Online method	Continuously measuring and registering systems. Nowadays, they are automated and are preferably used in industrial-scale plants.
Operating method	Simplified analysis method that can be applied with basic knowledge of analytical chemistry in order to obtain measurement results which are equivalent to standardized procedures. Operating methods are not approximative methods!
Organic layer	Growth or film of micro-organisms on surfaces of carrier materials
Oxygen demand level	The oxygen demand level rates residual organic pollution in the treated wastewater. Important parameters are biochemical oxygen demand BOD_5, chemical oxygen demand COD and ammonia nitrogen NH_4-N
P	
P phrase	P phrases (precautionary statements) provide safety notes
PAH	Abbreviation for “Polycyclic aromatic hydrocarbons”. The reference substance is benzo(a)pyrene, a carcinogenic compound. Determination is carried out by chromatography.
Parallel examination	Parallel analysis of a split sample with operating and reference methods
Pascal	Physical pressure unit. One pascal is the pressure caused by a force of one Newton onto a surface of one square meter.
PBT	Abbreviation for Persistent, Bioaccumulative, Toxic. This refers to particularly dangerous chemicals.
PCB	Abbreviation for “Polychlorinated biphenyls”, for which a carcinogenic effect was observed. PCBs are contained, inter alia, in coolants, hydraulic fluids and oils. PCBs are chemically and thermally relatively stable.
PCP	Pentachlorophenol, effective for protecting materials (especially wood) against mildew and rot. By now banned as a wood preservative.
Percent (%) as indication of concentration	Indicates the mutual weight ratio of two or more substances. 100 % corresponds to 1,000,000 ppm, 1 % thus to 10,000 ppm, 0.01 % = 100 ppm
Pesticides	Chemical agents for plant protection and pest control.
pH	Negative decadic logarithm of hydrogen ion concentration (or rather hydrogen ion activity). From the pH, the hydrogen and hydroxide ion concentrations can be calculated. Numerous photometric tests are strongly pH-dependent. Each integer pH step is an order of magnitude of hydrogen ion concentration.

Dictionary water analysis	
Phenol index, total	Cumulative parameter. Phenols are coupled under suitable reaction conditions to azo dyes that are evaluated photometrically.
Photometric accuracy and reproducibility	Technical details of photometers. Thus, possible deviations of the photometer during repeated measurements are detected (using a standard and a specified wavelength range). The value is given in percent (%). Nowadays, <1 % are typical.
Photometry	Analytical method for determining the concentration of colored solutions using light. Measurement of the absorption of monochromatic radiation by a colored solution.
PNOC	Particulates not otherwise classified
POC	Abbreviation for polyoxycarboxylic acid. Polyoxycarboxylic acids are used as inhibitors in water treatment.
Polluter-pays principle	Term often used in the amendment of laws. It says, in essence, that the costs must be paid by those who pollute the environment.
ppm	Abbreviation for “parts per million”, for solutions corresponding to the unit mg/L or g/m^3. 1 ppm is one particle among 1 million other particles.
Precipitation	Solutes are removed from a solution by addition of suitable substances, but also by heat and cold. Examples for this are calcium precipitation in metal analysis by sodium sulfate and clarification precipitation of nitrite-containing samples using Carrez solution. The solutes are thereby totally or partially converted into an insoluble precipitate, which then can be removed by filtration or centrifugation.
Precision	Measure of agreement between the results, as obtained with repeated measurements (scattering). It indicates how reproducible an analytical result is, but is not a measurand. Precision is expressed by means of statistical indicators. The coefficient of variation is such a precision indicator.
Preparation	The German Chemicals Act (most recently amended in June 2014) defines preparations as “mixtures or solutions consisting of two or more substances”.
Priority hazardous substances	Subset of the list of priority substances with increased hazard potential
Priority Substances	Priority substances are substances that pose a significant threat to the aquatic environment. The danger of these substances is on the one hand based on their ecotoxicological and human toxicological effects and on the other on their wide distribution and water pollution. A “priority list” is currently discussed in the European Water Framework Directive.
Procedure characteristics	Characteristics that allow assessment of the precision and correctness of a method.
Q	
Quality assurance	System to check the individual operating mode in terms of performance of analyses equipment and reagents. In this way errors can be determined or located. See *NANOCONTROL*
R	
Raw sludge	Raw sludge is sludge removed from wastewater treatment systems without prior treatment – German Sludge Ordinance (most recently amended in February 2012).
REACh	REACh = Registration, Evaluation, Authorisation and Restriction of Chemicals. Simplifies the chemicals legislation and is valid in all EU countries
Recalibration	Determination of the evaluation function of the analysis method at the present time of measurement. Control of calibration, taking into account the chemicals used (blank) and a synthetic matrix (reference) and the device status
S	
Sample preservation	Action to substantially prevent further alteration of parameters by chemical and bacteriological processes. It is done in a parameter-specific manner and is the more important, the further the analysis progresses to trace levels. Not all parameters can be suitably preserved; analysis should therefore be carried out as quickly as possible.
Sampling	The first and most essential step in determining content. The correct analysis result is significantly influenced by the sampling. Mistakes made here may be higher by “orders of magnitude” than those of the subsequent steps. Today increasingly parameter-specific sampling is required.
Screening test	Preliminary test (selection test) for rough classification
Secondary treatment	Wastewater processing by biological treatment with a secondary settler or other process in which the requirements are met (From: Council Directive on Municipal Waste Water Treatment)
Sedimentation	Settling of solid particles from a suspension, caused by the greater density and gravity of the solid. Sedimentation equilibrium and a specific height distribution of the particles are formed.
Sedimentation test, sedimentable solids	Determination of suspended solids within a specified time in the Imhoff cone.
Selectivity	In analytical reactions: Term that describes a limited number of reactive substances. A reaction is called specific if only one compound reacts. By addition of masking agents, selectivity can be increased.
Sewage sludge	Sludge produced in the treatment of waste water. It can be dewatered and dried. Spreading onto agricultural and forestry soils is subject to the German Sludge Ordinance. Treated or untreated sludge from municipal wastewater treatment plants. (From: Council Directive on Municipal Waste Water Treatment)
SI unit	International System of Units or SI (fr. Système International d’unités) – system of units of physical quantities
Solution	Homogeneous (same type) mixture of different substances in mutual penetration and fragmentation, generally down to the level of molecules, atoms or ions (true solution).

Dictionary water analysis	
Spiking	Term from the standard addition method. To a real sample, once or several times the substance of interest is added in a known concentration. Systematic or proportional errors, respectively, can be detected from the recovery rate.
Standard	Sample solution with a precisely known content of a substance or mixture. The concentration is usually near the middle of the useful range of a test.
Standard addition	Method for detecting proportional errors in a selected analysis. Principle: Spiking and determination of the recovery rate
Standard deviation of the procedure	Absolute measure of precision. Quality measure for the scattering of a test method
State of the Art	The federal and state governments of Germany use this term to denote the developmental stage of advanced processes, equipment and operations that provide the best possible limitation of emissions and thus help to secure protection of the aquatic environment without detrimentally affecting it.
Surfactants	See detergents
Suspended matter	Solids in the water which sink to the ground after a certain period of suspension.
Suspension	From suspendere (lat. = to hang, to suspend). Dispersed (finely distributed) system of insoluble (solid) particles in fluids: Subdivision into fine (< 100 mm) and coarse (> 100 mm) suspensions
T	
TC	TC = total carbon; the sum of all organically and inorganically bound carbon in a water sample in the form of dissolved and insoluble compounds.
Test cuvette	Test vessel in water analysis, e.g. photometry. There are round and rectangular cuvettes, made of various materials and in various sizes.
Test cuvette size	Term for the inner diameter of the cuvette used, typically 14 mm internal diameter for round cuvettes and 5, 10, 20 and 50 mm for rectangular cuvettes.
TIC	TIC = total inorganic carbon, consisting of dissolved carbon dioxide, hydrogen carbonate and suspended carbonate.
TIC	Technical indicative concentration: Concentration of a substance in the workplace air that can be achieved according to the state of the art.
Titration	Volumetric method for determination of a specific material content in a solution
TOC	TOC = total organically bound dissolved and insoluble carbon. Guide value for the total content of organic compounds; the dissolved fraction corresponds to the DOC value.
Total metal	Sum of all chemical compounds of a metal including ionic, complex, colloidal or insoluble portions
Total nitrogen	Various definitions exist. In general, the sum of organic nitrogen, ammonium, nitrate, nitrite. In wastewater legislation, organic nitrogen is still only partially considered.
Toxicity	Toxicity is the poisonous effect of specific substances or rays on humans, animals and plants. It is e.g. indicated in the form of lethal dose LD_{50}, lethal concentration LC_{50} or effective concentration EC_{50}. Acute toxicology (one-time uptake causes toxic effects), sub-acute toxicology (the toxic effect sets in only after repeated uptake over a certain period) and chronic toxicology (toxic effects over longer periods) are distinguished.
Trace analysis	Presently approximately the range ≥ 0.001 mg/L is covered by photometry when using rectangular cuvettes
Transparency	Among other things, a concept in photometry. The ratio of the intensities of incident and exiting light is called permeability or transparency T. The transparency of a solution is 100 % minus the absorption.
Trophic level	Degree of supply of an ecosystem with nutrients. Oligotrophic: low nutrient supply; mesotrophic: moderate nutrient supply; eutrophic: good nutrient supply
TTC	2,3,5-triphenyl tetrazolium chloride. Basis of the *NANOCOLOR*® TTC test
TTC method	Determination of dehydrogenase activity (DHA). Test method for determination of sludge activity. Reaction of colorless 2,3,5-triphenyltetrazolium chloride to deep red 1,3,5-triphenyl formazan. This method allows e.g. conclusions on possible disturbances of the biology of a wastewater treatment plant.
TU/F	Turbidity unit formazine (see FAU / FNU)
U	
UN number:	Number on the list of all dangerous goods, substances and groups compiled by an expert committee of the United Nations
UV/VIS	UV/VIS spectroscopy (ultraviolet and visible spectroscopy) in the wavelength range from about 1 nm to 400 nm
V	
Validation	The term validation is derived from validus (lat.); validum facere = to make valid. The term standard DIN EN ISO 8402:1995 (section 2.18, p.14) notes on validation: “Confirmation by examination and furnishing of evidence that the particular requirements for a specific intended use are fulfilled.” Control and documentation that equipment and systems are functional. Documented evidence of suitability for the performance of certain tasks
VIS	Visible spectroscopy = spectroscopy in the visible wavelength range of about 350–700 nm.
VISOCOLOR®	Colorimetric and titrimetric analysis system by MACHEREY-NAGEL, which can partially be evaluated photometrically.
W	

Dictionary water analysis	
Wastewater	Runoff water altered by use, and any water entering into the sewage. This includes waste water, rain water, infiltration water, mixed water and cooling water.
Water hardness	Content of calcium and magnesium salts (alkaline earth metal ions) in water. Calcium hardness and magnesium hardness can be distinguished. Calcium and magnesium hardness = total hardness Guide values: · 3 °d = soft water · 14 °d = moderately hard water · 21 °d = very hard water
Water quality	Classification of water bodies from a biological perspective. Currently, 4 classes are common: Quality class 1: not or only slightly polluted Quality class 2: moderately polluted Quality class 3: heavily polluted Quality class 4: very heavily polluted
WHC	Water hazard classes, in Germany from 0 to 3: · WHC 3 = highly polluting substances · WHC 2 = polluting substance · WHC 1 = slightly polluting substance · WHC 0 = non-polluting substance

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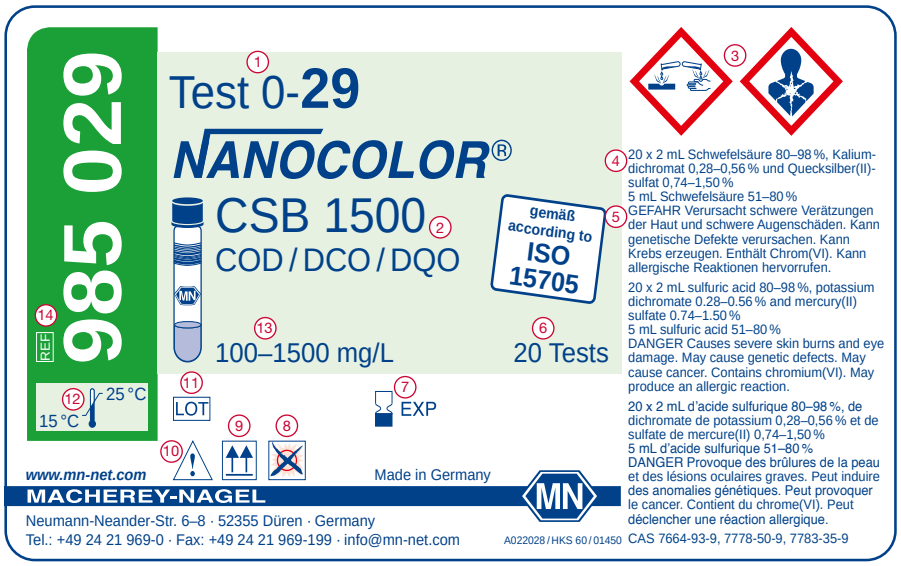
7.4 Important information on the *NANOCOLOR*® label



1. Test number
2. Test name and parameters
3. Hazard icons
4. Included chemicals
5. Signal word and H statements
6. Number of tests contained
7. Date of expiry
8. Do not expose to direct sunlight
9. Store package upright
10. Caution under GHS: Additional GHS information in the package insert
11. Batch number
12. Storage temperature
13. Measurement range
14. REF = item #

7.5 Explanation of the icons used

Icon	Explanation
	Background information
	Important information
	Chemical information
	Legend for the diagram
	Definitions, formulas or illustrations
	Available for download
	Link to the website of MACHEREY-NAGEL

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